A STUDY OF SOME COMPLEXES OF THALLIUM AND TELLURIUM

BY

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SUMMARY

Complexes of the type TlX_3L (where L = bipy, phen, dipyam etc. and X = Cl and Br) were prepared together with some new complexes with the terdentate ligand tri-(2-pyridyl)amine. When the above complexes were recrystallized from dimenthylformamide (DMF) a new series of complexes with co-ordinate DMF were obtained. The structure of TlX_3(tripyam) was obtained with the help of ^1H nuclear magnetic resonance, diffuse reflectance spectroscopy and infra-red spectroscopy. The structure was "octahedral" with C_{3v} symmetry. The structure of the complex TlX_3 (tripyam) DMF was also deduced. When DMF was co-ordinated into the octahedral sphere, the terdentate tri(2-pyridyl)amine opened to become a bidentate base. The infra-red and ^1H n.m.r. spectra were produced in evidence for the co-ordinated DMF and also for the bidentate tri-(2-pyridyl)amine base. The structure of the TlX_3(chelate) were also obtained with the help of far-infra and Raman vibrational spectroscopy and of a chemical approach. The evidence suggested polymeric structures for the complexes. The finding is renewed in the light of recent X-ray studies with Tl(phen)Cl_3 and the difficulties of interpreting vibrational spectroscopic data for the complexes of heavy metals is stressed.

The thallium (I) complexes with bipy,phen, thiourea and substituted thioureas were prepared. The structure of the thallium (I) complexes with the nitrogen donor ligands is believed to be relatively undistorted. Some new complexes of thallium (I) with substituted thiourea were obtained and the possible assignments are suggested.

The organotellurium compounds with the formula R_2Te and R_2TeX_2 (where R = phenyl, o-tolyl, p-tolyl, p-methoxyphenyl, p-ethoxyphenyl and X = Cl, Br and I) were prepared. Some new compounds such as the di(perfluorophenyl) tellurium dihalides and dibenzyltellurium dihalides were prepared. The far infra-red and Raman spectra of the above compounds were obtained and discussed in detail. The low frequency infra-red and Raman spectra were assigned for the diaryltellurium dihalides. The spectra of the above compounds suggested that the basic ψ- trigonal bipyramidal structure is common to all compounds. Dibenzyltellurium dihalides were prepared to study ^{1}H n.m.r. spectra but no coupling of the methylene group with ^{125}Te was seen. Attempts were made to prepare telluroylids. Some use of diaryltelluride were investigated with the possible catalytic use of the diaryl telluride.

The possible use of organotellurium compounds as dehalogenating agents or dehalogenodimerisation agents was investigated but it was found that the compounds offer no particular advantage over other reagents.

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A SPECTROSCOPIC INVESTIGATION OF SOME COMPLEXES OF THALLIUM

CHAPTER I

INTRODUCTION

For many years any complexes of non-transition elements which were prepared were studied only by molecular weight determination, conductivity measurements and often wrong conclusions were drawn about their solid state structures. Now there are new physical techniques of measurement available such as infra-red spectroscopy, Raman spectroscopy, nuclear magnetic resonance spectroscopy (n.m.r.), electron spin resonance spectroscopy (e.s.r.) and Mössbauer spectroscopy, which can sometimes help to determine the solid state structures of non-transition element complexes.

In a nuclear magnetic resonance (n.m.r.) experiment recognition of chemical shifts has developed the technique into a tool for research into the structure of matter. Chemical shift data have been reported for numerous compounds of several elements and have been shown to be useful for the qualitative and semi-quantitative study of molecular bonding. Rowland and Bromberg [1] were able to measure the chemical shift of ^{205}Tl in a number of thallium compounds in the molten state. They reported chemical shift data in the liquid and solid phase for $TlNO_3$, TlCl, Tl_2X_4(X = Cl & Br). In the case of Tl_2X_4 they found that the compound might have the structure $TlX.TlX_3$. In view of the evidence that two distinct species of thallium ions are present in these salts, thallous and thallic, one might expect two distinct thallium resonance peaks to be present in the resonance spectra of the molten compounds. Indeed Rowland and Bromberg found two resonance peaks in each complex salt and also the shifts between the two peaks were, in both cases, temperature dependent, decreasing with increasing temperature. Freeman, Gassar and Richards[2] also measured the chemical shifts of thallium salts in their solid state. They also discuss the resonance spectra of ^{205}Tl in aqueous state. Hafner and Nachtrieb[3] also worked with n.m.r. chemical shifts of thallium salts. They found that the thallium resonance frequency in both crystalline and molten thallium salts, showed a remarkable progression in the order $\bar{I} > \bar{Br} > \bar{Cl} > NO_3^-$. This sequence shows that the paramagnetic shielding effects are large for ligands which produce a small electric field. Thallous fluoride occupies a position between TlBr and TlCl, indicating that the electron affinity of the halogen atom rather than its electro-negativity is the important factor.

The discovery of Mössbauer spectroscopy helps the Inorganic Chemist to solve structural problems. Mössbauer spectroscopy has been used to obtain the information of the nature of bonding between a metal atom and its ligand, the structure of metal ligand complexes, the identification of different oxidation states of the element in their compounds, in the studies of crystal structure, ionic state, electron density, and the magnetic properties of the material. Mössbauer spectroscopy so far is only widely used in the fields of iron and tin chemistry but there are other elements where the Mössbauer effect was found including tellurium. The technique has been widely used in studying the magnetic field of binary metallic compounds and alloys. Both magnitude and the sign of the internal field can readily be found in this way. The internal magnetic field nuclear may be either increased or decreased by an externally applied magnetic field. To date no application of Mössbauer spectroscopy to organotellurium compounds has been made.

Thallium is a classic example of post transition group element, for which two oxidation states are well known. Thallium (1) forms very few complexes and this oxidation state is thermodynamically more stable than thallium (III).Thallium (III) forms many more complexes whose co-ordination numbers vary from four to six. Solid state structures have not in many cases been unambigously determined. Thallium (III) halide complexes are good examples of this and a number of the type TlX_3L (where X = Halogen, and L = one bidentate or two monodentate ligands) have been prepared. Most of the above type complexes have been prepared with a nitrogen donor ligand such as pyridine (Py), 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), 2,2',2" terpyridyl (terpy) and di-(2-pyridyl)amine (dipyam).

Sutton[4.5] prepared a number of new complexes of the thallic halides with nitrogen donor chelating ligands. He prepared TlX_3(bipy) and TlX_3 (Phen) (X = Cl, Br.I) by adding the appropriate amount of an alcoholic solution of ligand to the thallic halide tetra hydrates dissolved in water. TlI_3 (bipy) and TlI_3(phen) were prepared by the reaction with a solution of sodium iodide during the preparation of $TlCl_3$ (bipy) and $TlCl_3$(phen). Sutton[5] made conductivity and molecular weight measurements on a number of the above thallic halide complexes including ethylenediamine (en). The conductivity measurements in nitrobenzene showed that the TlX_3L (L=bipy, phen and en) were 1:1 electrolytes in solution. He suggested that a possible structure for the above complexes could be:

$$[TlX_2L_2]^+ \ [TlX_4]^-$$

This conductivity measurement did not prove this dimeric ionic structure for solid state, but only in solution ionic species were formed which gave a conductance somewhat less than typical values for 1:1 electrolytes.

Kul'ba[6] and his co-workers prepared Tl(III) halide complexes with pyridine and quinoline. Although the pyridine complexes of thallic halides were known for many years. Meyer[7], Renz[8] and Krause and Gresse[9] prepared these complexes but no systematic structural studies were made. Kul'ba and his co-workers claimed that the reaction of thallic halide and dilute pyridine afford only one compound with the formula $TlX_3(Py)_2$, and they reported that $TlX_3(Py)_3$ was only obtained when thallic halide was reacted with pure pyridine. Later Kul'ba and co-workers[10] made conductivity measurements on the above complexes. The complexes were hydrolysed by even trace amount of water, therefore they used methanol and nitrobenzene as solvent. The values of the molar conductance of $TlX_3(Py)_2$ (where X=Cl, Br) were very near to 1:1 electrolyte. The conductivity measurement of $TlI_3(Py)_2$ in nitrobenzene was difficult, as the compound was decomposed in the nitrobenzene and in methanol, but in acetone the decomposition was very slow and the compound has the molar conductance value very close to that of 1:1 electrolyte. The 1:1 electrolytic formulation of above complexes was also supported by the migration of an anion and a cation of the above complexes in methanol solution. Electrolysis of $TlCl_3(Py)_2$ and $TlCl_3(Py)_3$ in methanol showed that the thallium and halide ions were present in both anion and cation. So Kul'ba and his co-workers formulated the structure of the above complexes as

$$[TlX_2(Py)_2]^+ \; [TlX_4]^- \quad \text{for } TlX_3(Py)_2$$

and

$[TlX_2(Py)_4]^+$ $[TlX_4(Py)_2]^-$ for $TlX_3(Py)_3$

These structures supported the views expressed by Sutton[5] that the TlX_3(bipy), TlX_3(phen) and TlX_3(En) complexes were 1:1 electrolytes. Two molecules of pyridine replace by one molecule of one of the bidentate ligands.

Cotton, Johnson and Wing[11] prepared TlX_3L (where L = 2,2' bipy, 1,10 phen, 2Py, 3Py and X = Cl,Br and I) complexes and a number of other thallic halide complexes with various neutral ligands e.g. dimethyl sulphoxide (DMSO), triphenyl phosphine oxide etc. Instead of using $TlX_3.4H_2O$ as a starting material, which is thermodynamically unstable with respect to thallium (I) halides and particularly prone to hydrolysis, they prepared thallic halides in a non-aqueous solvent such as acetonitrile (CH_3CN). Thallic halides were prepared by suspending thallous halides in acetonitrile and oxidising with chlorine or bromine; ethanolic solution of appropriate ligand was then added. They also prepared pyridine complexes with thallic chloride and agreed with Kul'ba[6] and his co-workers that only one compound with the stoichiometry $TlCl_3(Py)_2$ was formed when dilute pyridine solution was used. The conductivity measurement of the above complex in acetonitrile showed that the molar conductance of 107 Ohm^{-1} cm^2 $mole^{-1}$, which was somewhat low for the formula $[TlCl_2(Py)_2]^+$ Cl^- and it was a little high for the $[TlCl_2(Py)_4]^+$ $[TlCl_4]^-$ for expected 1:1 electrolyte (the range for 1:1 electrolyte in acetonitrile is 120-160 Ohm^{-1} cm^2 $mole^{-1}$) [12]. But Cotton and his co-workers agreed with Kul'ba that the structure of the above complex may be either of these two. The conductivity measurement of $TlCl_3$(phen) also in acetonitrile shows the molar conductance of 52 Ohm^{-1} cm^2 $mole^{-1}$ for the formula $TlCl_3$(phen) or twice for a dimer $[Tl(phen)_2Cl_2]^+$

$[TlCl_4]^-$ which was a little bit low for the ionic formula for 1:1 electrolyte. They agreed with the ionic dimeric structure suggested by Sutton[5].

McWhinnie[13] prepared TlX_3L type compounds with thallic halides. He also reported the preparation of the new complexes of thallic halide with di-(2-pyridyl)amine(dipyam) with the formula TlX_3L. He reported conductivity measurements and infra-red spectra as nujol mulls, and acetone and pyridine solution spectra for $TlCl_3(Py)_2$. Also some solid state spectra of TlX_3(bipy), TlX_3(phen), $TlCl_3$(dipyam) were reported. He made conductivity measurements on $TlCl_3(Py)_2$ in acetone and found the molar conductance values of 63 Ohm^{-1} cm^2 $mole^{-1}$ in approximately 10^{-3} M solution. The conductance value was very low for the monomeric formula $[TlCl_2(Py)_2]^+ Cl^-$ but very close for the ionic dimer $[TlCl_2(Py)_2]^+[TlCl_4]^-$ for the 1:1electrolyte. The solution spectra of the above complex in acetone was in excellent agreement with the presence of $TlCl_4^-$ ion present in solution. This is supported by Spiro's[14] work on the Raman spectra of Tl(III) halide species such as

$$TlCl^{2+}, TlCl_2^+, TlCl_3, TlCl_4^-$$

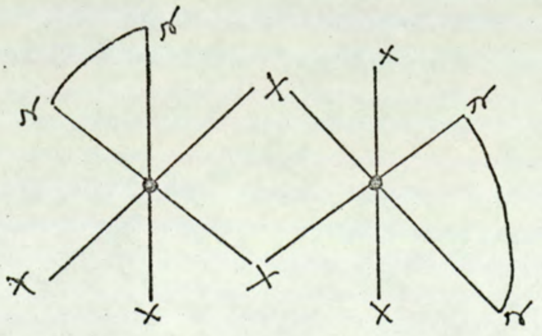
in aqueous media, where the Raman active band shifts to lower frequency as the positive charge decreasing. In the case of solution spectra of $TlCl_3(Py)_2$ in acetone the thallium chlorine stretching frequency of cationic species would be expected at higher wave number than that of an ionic species. McWhinnie reported the single band located at $381cm^{-1}$ to be assigned as a thallium chlorine stretching frequency of $TlCl_2(Py)_2^+$ ion, and the bands at about $295cm^{-1}$ to be assigned as thallium chlorine stretching frequency of $TlCl_4^-$ unit. The solid state spectra of the above complex was different than that for solution, and the dimeric formulation did not support the solid state structure. The conductivity measurements were not reported for TlX_3L (where L = bipy, phen, dipyam etc), the solid state spectra of the above complexes were reported as nujol mulls. The spectra for TlX_3L did not support the dimeric formulation since assignment of the highest frequency modes at 290cm^{-1} to $TlCl_4^-$ unit required unrealistically low frequencies to be assigned to $[TlCl_2L_2]^+$, which should be at a higher frequency than that for $TlCl_4^-$ unit. With some reservation he put forward the suggestion that the solid state structure of the above complexes would be similar, as the general profiles of the solid state spectra were similar.

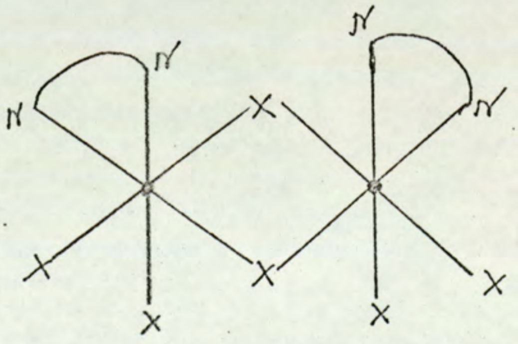
Walton[15] who had been very active in this field of chemistry with Johnson[16] for some time, followed up his previous work on thallium(III) and indium(III) halides complexes with nitrogen donor ligands. He prepared some new complexes with terdentate ligand 2,2',2"- terpyridyl and measured conductivity and a infra-red spectra in detail. With detailed molecular weight determination and conductivity measurements in different solvents at different concentrations, he concluded from the result that for many thallium (III) halide complexes there was a tendency for them to undergo dissociation in most solvents. The results also showed that the thallium (III) halide complexes did not obey the Onsagar law of electrolyte. Thus weak electrolyte behaviour in solvent such as acetonitrile, acetone and nitromethane was discussed. The conductivity measurement in different solvents and at different concentration, the typical compound such as $(C_6H_5)AsTlCl_4$ behaves as a 1:1 electrolyte while the compound such as $TlCl_3(Py)_2$, $TlCl_3(bipy)$ etc. behave as a weak electrolyte. The $TlCl_3(Py)_2$ forms a non-conducting solution in acetone, although the conductance was markedly increased as the concentration of the solution decreased below 10^{-3}M. Similar observations were made for the complexes of pyridine and $TlX_3(bipy)$ (X = Cl&I) in acetonitrile solution. Walton ruled out the dimeric structure of pyridine complex on the basis of concentration range conductivity, which showed the characteristic weak electrolyte.

In the same paper Walton[15] reported the solid state spectra of $TlCl_3(Py)_2$ and found that it has its highest thallium chlorine stretching frequency, ν(Tl - Cl) mode at 268 cm^{-1}. So he suggested that the above observation ruled out the ionic structure $[(TlCl_2(Py)_2]^+ Cl^-$, $[TlCl_2(Py)_4]^+ TlCl_4^-$ $[TlCl_2(Py)_2]^+ [TlCl_4(Py)_2]^-$ and five co-ordinate $TlCl_3(Py)_2$. He suggested that the above complex might be a halogen bridged dimer or polymer in solid state. The solid state spectra of $TlCl_3$(bipy) was similar to the $TlCl_3(Py)_2$ but it was more complex than the later one, also the highest ν(Tl-Cl) mode appeared at higher frequency. The complexity of spectra and the conductivity measurement ruled out the ionic structure $[TlCl_2(bipy)]^+ Cl^-$, $[TlCl_2(bipy)_2]^+[TlCl_4]^-$, $[Tl(bipy)_2]^{3+}$ $[TlCl_6]^{3-}$ and five co-ordinate $TlCl_3$(bipy). He made suggestions that the above complex might have the structure similar to $TlCl_3(Py)_2$, a halogen bridged dimer or polymer. $TlCl_3$(Phen) complex showed similarity in conductivity and in an infra-red spectra, and halogen bridged dimeric or polymeric structure was also suggested for it. Walton reported new complexes of thallium (III) halides with the terdentate ligand 2,2', 2" terpyridyl with the ratio of 1:1 and 2:1. Thallic chloride formed complexes with formula $TlCl_3$(terpy) (terpy = 2,2', 2" terpyridyl) and $(TlCl_3)_2$ terpy while the thallic iodide complex with the formula $(TlI_3)_2$ terpy only. The conductivity measurements in the concentration range 10^{-2}M and 10^{-3}M, the $(TlX_3)_2$ terpy (X = Cl,I) and TlI_3Py showed the molar conductance, characteristic of 1:1 electrolyte in acetonitrile, although below 10^{-4}M concentration significant deviation was observed from the Onsagar law of electrolyte. Walton proposed the structure of the above complexes as ionic $[TlX_2(Terpy)]^+$ $[TlX_4]^-$ and $[TlX_2(Py)_2]^+$ $[TlX_4]^-$ in solution but he hesitated to draw any firm conclusions about their solid state structures. The infra-red spectra of the $(TlX_3)_2$ terpy in the region 320-250 cm^{-1} and 190-90 cm^{-1} might be convincingly assigned on the basis of the proposed ionic structure. He assigned the bands at 318cm^{-1} and 308 cm^{-1} of thallium chlorine stretching frequencies ν(Tl-Cl), for the $TlCl_2{}^+$ ion and at 277cm^{-1} and 270cm^{-1} of ν(Tl-Cl) for the $TlCl_4{}^-$ ion, also a band at 186cm^{-1} of thallium iodine stretching frequency ν(Tl-I) for a $TlI_2{}^+$ ion and 150cm^{-1} and 138cm^{-1} of ν(Tl-I) for a $TlI_4{}^-$ ion. Although the $TlCl_4{}^-$ bands were at considerably lower frequency compared to $(C_2H_5)_4N\ TlCl_4$ and $(C_6H_5)_4AsTlCl_4$ which gave bands at 290cm^{-1} for $TlCl_4{}^-$ ion. The spectrum of $(TlCl_3)$ (terpy) in acetonitrile showed a band at 311cm^{-1}(sh) and 293cm^{-1}, which were probably ν(Tl-Cl) for $TlCl_2$ and $TlCl_4{}^-$ respectively. The later band at 294cm^{-1} was very close to the band 295cm^{-1} for $(C_6H_5)_4AsTlCl_4$ reported by McWhinnie[13] in acetonitrile. So the infra-red spectra in the solid state and in the solution supported the ionic formulation for the species in solution as well as in solid state.

More recently Walton[16] has reported a new data for thallium (III) halide complexes with a complete study of infra-red and Raman spectra. In the case of $TlCl_3(Py)_2$ and $TlCl_3(Py)_3$, the Raman and infra-red spectra were very similar to each other and he suggested that both complexes might have a similar structure. He reported that the Raman spectra of the $TlCl_3(Py)_2$ showed the absence of a very intense band at about 312cm^{-1} characteristic of the $TlCl_4{}^-$ anion and none of the other bands were at sufficiently higher frequencies to be assigned for $[TlCl_2(Py)_4]^+$ cation. So from the data he ruled out the ionic structure $[TlCl_2(Py)_4]^+\ TlCl_4{}^-$ and $[TlCl_2(Py)_2]^+\ Cl^-$. The highest thallium chlorine stretching frequency of $TlCl_3(py)_3$ was about 15cm^{-1} lower than the related $InCl_3(Py)_3$[17,18]. Walton suggested a similar cis-octahedral structure to $TlCl_3(Py)_3$ and related γ- picoline adduct. Also the Raman and infra-red spectra of $TlCl_3(Py)_2$ were very similar to $TlCl_3(Py)_3$ and vibrational spectra of the former complex reveals marked infra-red and Raman co-incidencies, so he believed that $TlCl_3(Py)_2$ was a non-centrosymmetric six co-ordinate halogen bridged dimer.

Walton[16] also reported the Raman spectra of $TlCl_3L$ (L = bipy & phen) and it showed an absence of an intense Raman band at about 312cm^{-1}, a characteristic band of $TlCl_4^-$ anion[14], hence both the complexes did not have the ionic structure $[TlCl_2L_2]^+ [TlCl_4]^-$. Also he ruled out the other ionic possibility $[TlCl_2L]^+ [TlCl_4L]^-$ because the thallium chlorine stretching frequencies of the four co-ordinated cation should occur at significantly higher frequencies than that for $TlCl_4^-$ anion. In case of $GaCl_3$(bipy), Carty[19] suggested that the above complex might have an ionic structure $[GaCl_2(bipy)_2]^+ [GaCl_4]^-$ on the basis of detailed far infra-red spectra and later Restivo and Palenik[20] confirmed the dimeric ionic structure by X-ray crystallography. Walton observed the highest thallium chlorine stretching frequency ν(Tl-Cl) 25-30cm^{-1} above those of six co-ordinate derivatives $TlCl_3(Py)_2$ and $TlCl_3(Py)_3$. This at first suggested that the $TlCl_3$(bipy) and $TlCl_3$(phen) might be five co-ordinated monomers, but since he observed four distinct vibrational frequencies assigned to ν(Tl-Cl), where as for the five co-ordinated monomer $TlCl_3L$, a maximum of three were possible. So he favoured the six co-ordinated non-centrosymmetric halogen bridged dimeric strucutre of the type $LCl_2TlCl_2TlCl_2L$





While $TlCl_3L$ (L = bipy and Phen) have no ionic formulation according to Walton, he assumed that $TlBr_3L$ and TlI_3L would have the ionic structure. Walton argued that the Raman spectra and infra-red spectra of $TlBr_3L$ and TlI_3L showed vibrational frequencies characteristic of the $TlBr_4^-$ and TlI_4^- anions. For the known Gallium and Indium cationic and anionic species, the frequency differences between the infra-red active ν_3 mode of tetrahedral $[MCl_4]^-$ and the highest ν(M-Cl) sketching frequency of $[MCl_2L_2]^+$ were +70 and +30 cm^{-1} respectively[16,19,21]. For the heavier thallium (III) halide species one might expect significant band overlapping to occur between the vibrational frequencies associated with the related cationic and anionic thallium (III) hallides, this becomes more likely for the above bromide and iodide complexes. Walton thus assigned a very intense Raman band at 137cm^{-1} to the Raman active ν_1 mode of TlI_4^- for the TlI_3(bipy) complex. The other band at a higher frequency at 165cm^{-1} was assigned to thallium iodine stretching frequency ν(Tl-I) for the cationic species $[TlI_2(bipy)_2]^+$. Walton suggested that the above complex might have a cis-$[TlI_2(bipy)_2]^+$ structure similar to its analogous cis $[InCl_2(bipy)_2]^+$ [17] cation. The TlI_3(Phen) showed similarity in the general profile of the spectra so the above cis-structure was suggested for it. Walton assigned the following bands for cation and anion of $TlBr_3$(bipy) and $TlBr_3$(phen), bands at 212 and 208cm^{-1} assigned for the cation $[TlBr_2(bipy)_2]^+$ and 199 and 190cm^{-1} for the anion $[TlBr_4]^-$ for the $TlBr_3$(bipy) complex and bands at 207cm^{-1} for the $[TlBr_2(phen)_2]^+$ and bands at 202 and 186cm^{-1} for the $[TlBr_4]^-$ for the $TlBr_3$(phen) complex. So far the above two complexes Walton suggested that both the complexes might have the similar cis$[TlBr_2L_2]^+$ type structure.

Thallium (I) which is thermodynamically very stable, forms very few complexes particularly with the nigrogen donor ligands. Thallium (I) nitrate and thallium (I) perchlorate form complexes with 1,10-phenanthroline and 2,2'-bipyridyl[22]. The complexes were found 1:1 electrolyte and thus $\mathrm{Tl(phen)_2^+}$ and $\mathrm{Tl(bipy)_2^+}$ ions were stable in solution[22]. However, it is not known whether the s^2 pair of electrons plays a stereochemical part in the structure of $\mathrm{Tl(phen)_2^+}$ and $\mathrm{Tl(bipy)_2^+}$ ions, as they are known to do in the compound such as $\mathrm{TeCl_4}$. The electron diffraction data[23] suggested that in the gaseous phase, tellurium tetrachloride has a trigonal bipyramidal structure in which one equatorial position is occupied by a lone pair of electron as shown in Fig 1.2

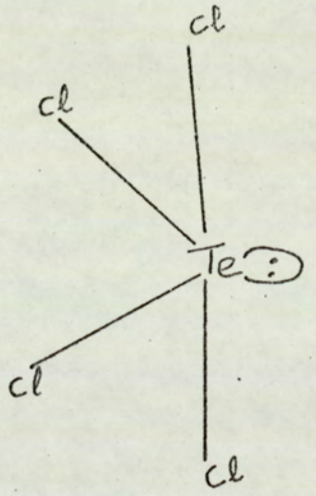
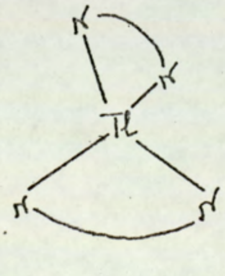
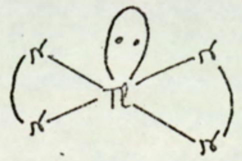


Fig. 1.2

For the $\mathrm{Tl(phen)_2^+}$ and $\mathrm{Tl(bipy)_2^+}$ ions, from the many possible structures, three typical structures are shown below in Fig 1.3





1.3a

1.3b

1.3c

1.3a is the case of pure s character in the $6s^2$ electron, where they play no stereochemical role and 1.3b and 1.3c are the possibilities where they do play stereochemical role. Chemical and spectroscopic apporaches have been made to resolve the problem.

One paper described the infra red spectrum of $Tl(Phen)_2ClO_4$ but no particular assignments have been made[24]. Also Kulba and his co-workers[25] reported the far infra red spectra of $Tl(Phen)_2NO_3$ and $Tl(Phen)_2ClO_4$ and they made thallium-nitrogen stretching frequency assignment at 250cm^{-1}, but no structural suggestion was made.

Thallium (I) complexes with sulphur donor ligands have been known for many years. In 1888 Reynolds[26] reported a crystalline complex containing NH_4Br and thiourea in the ratio 1:4. This was the first example of what is now known to be a large family in which some alkali halides and many thallium (I) salts can replace NH_4Br.

Thallium thiourea complexes were first prepared by Rossenheim and Loewnstumn[27]. Since then many other workers[28,29,30] prepared the above type of complexes with thallium (I) salts. But despite their relatively large number, nothing definite was known about the structure of these complexes nor about the nature of the bonding between their components. Cox, Shorter and Wardlaw[31] studied the $TlNO_3(4TU)$ and $TlCl(4TU)$ (TU = thiourea) complexes by x-ray analysis and suggested that in the four co-ordinate state, four valencies of the thallous atom are co-planar. But the above suggestion was ruled out by Boeyens and Herbstein[32]. By x-ray diffraction method they found that all the thallium (I) thiourea complexes have nearly similar structure. They suggested that the structure of the above complexes were polymeric with eight co-ordinate thallium atoms, as shown in the fig 1.4

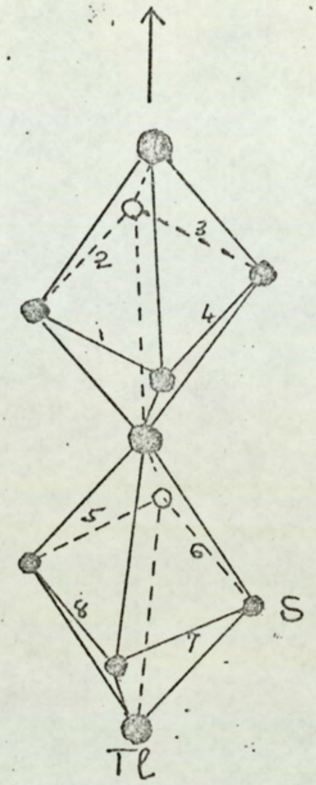


Fig. 1.4

This covers all the relevant work to date on the thallium (III) halide complexes and thallium (I) nitrogen donor and sulphur donor ligands complexes. Chemical and spectroscopic apporaches have been made to elucidate their structure.

CHAPTER 2

(a) PHYSICAL MEASUREMENT - EXPERIMENTAL

Infra red Spectra

Infra red spectra were recorded as nujol mulls on a P.E.237 spectrometer in the region 4000-625 cm^{-1} using sodium chloride windows. This was to establish that a complex had in fact been formed and also to give some indication of purity. A nujol mull was made by grinding a small amount of sample in an agate mortar with a drop of liquid paraffin. The mull was then transferred to the sodium chloride windows of a cell, placed in the instrument and the spectrum was run. The instrument was calibrated with standard polystyrene film.

All the thallium (I) complexes were also run as nujol mulls on the P.E.225, an instrument of superior resolution, over the region 4000-400cm^{-1} using potassium bromide windows, and from 410-200cm^{-1} using Caesium iodide windows. All other thallium (III) complexes were recorded on the P.E 225 and on a P.E.457 instrument in the region 4000-400 cm^{-1} using potassium bromide windows and in the region 400-200cm^{-1} using polythene windows, since thallium (III) is a strong oxidising agent, caesium iodide windows were unsuitable to use. Many tellurium compounds spectra were recorded by the potassium bromide disc technique in the region of 4000-400cm^{-1}. A potassium bromide disc was prepared by mixing a small amount of the compound with 0.2 to 0.3 gm. of dry potassium bromide and the mixture was ground in an agate mortar, and then placed in a special cell between two well polished metal dies. The mixture was then pressed with up to 15 tons pressure under vacuum. After 15 to 20 minutes the vacuum and the pressure were released and the disc was separated very carefully from the metal dies. The disc was then placed on a cell holder and the spectrum was run from 4000-250cm^{-1} on a P.E.457 instrument. One big advantage of this technique is that it gives only the spectrum of the compound and avoids all interference bands present when paraffin or hexachlorobutadiene are used as the matrix.

Far infra-red spectroscopy is of great interest to chemists, because from the low frequency vibrational spectra one can obtain information to perform full normal co-ordinate analyses, observe direct hydrogen bond stretching frequencies and elucidate molecular structure, especially of inorganic compounds. In recent years instruments for use in the far infra-red have become commercially available, but some of them are grating instruments and suffer from the disadvantages of grating instruments such as much of the initially weak light intensity originating in the source is lost through dispersion and diffraction, and the intensity of the radiation being received at the detection is greatly diminished. Also the cost of these grating instruments is very high. A new type of instrument, the interferometric spectrometer, is much more efficient in its use of the available light than the conventional instrument because it does not use gratings, prisms or narrow slits and is capable of affording excellent resolution.

There are several types of interferometers but all essentially have a coherent source, a beam splitter and a detection system. Since the techniques have been improved, commercial interferometers have become available from many firms. The typical diagram of the Research and

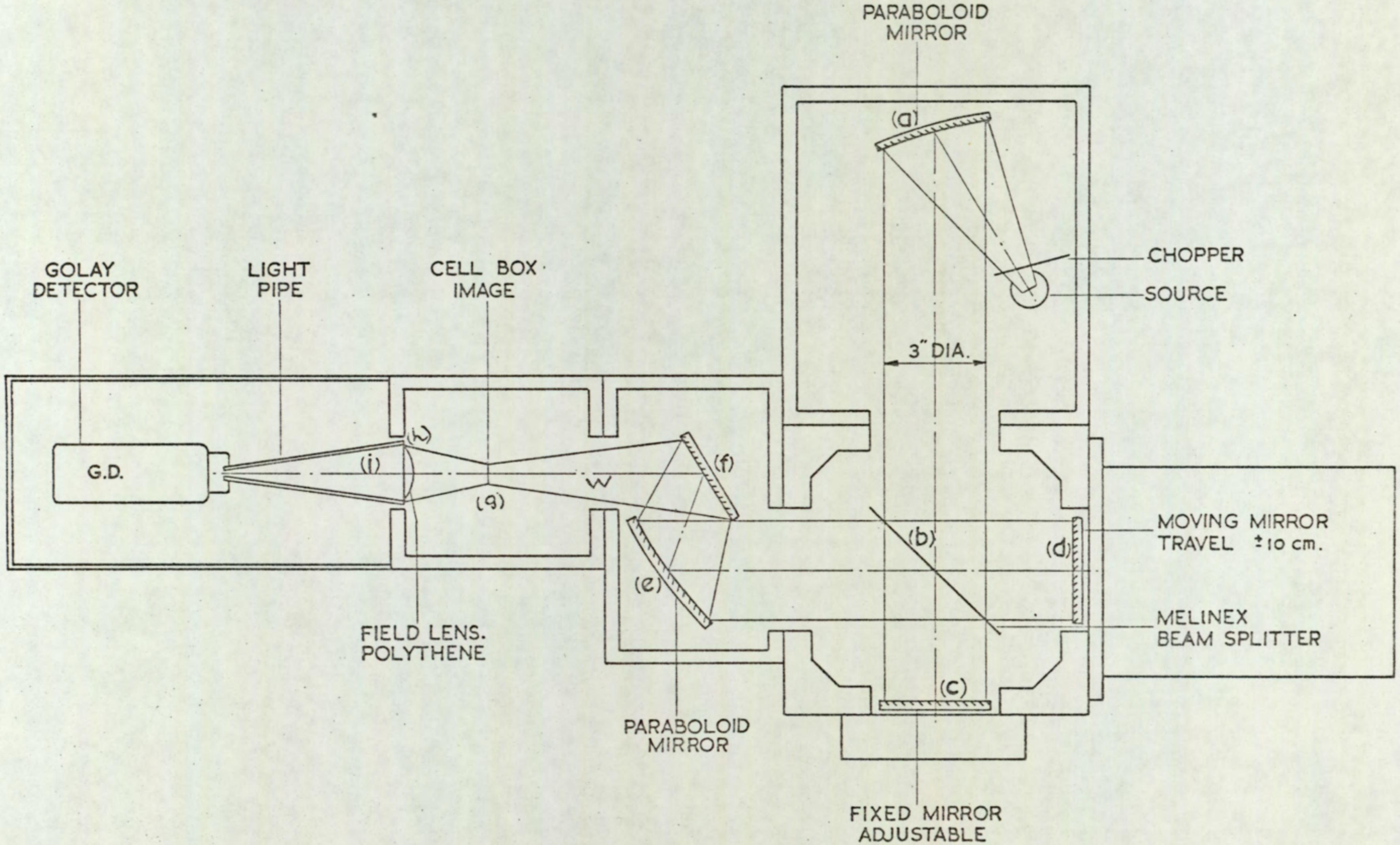


FIG.- 2-1 THE FOURIER SPECTROPHOTOMETER

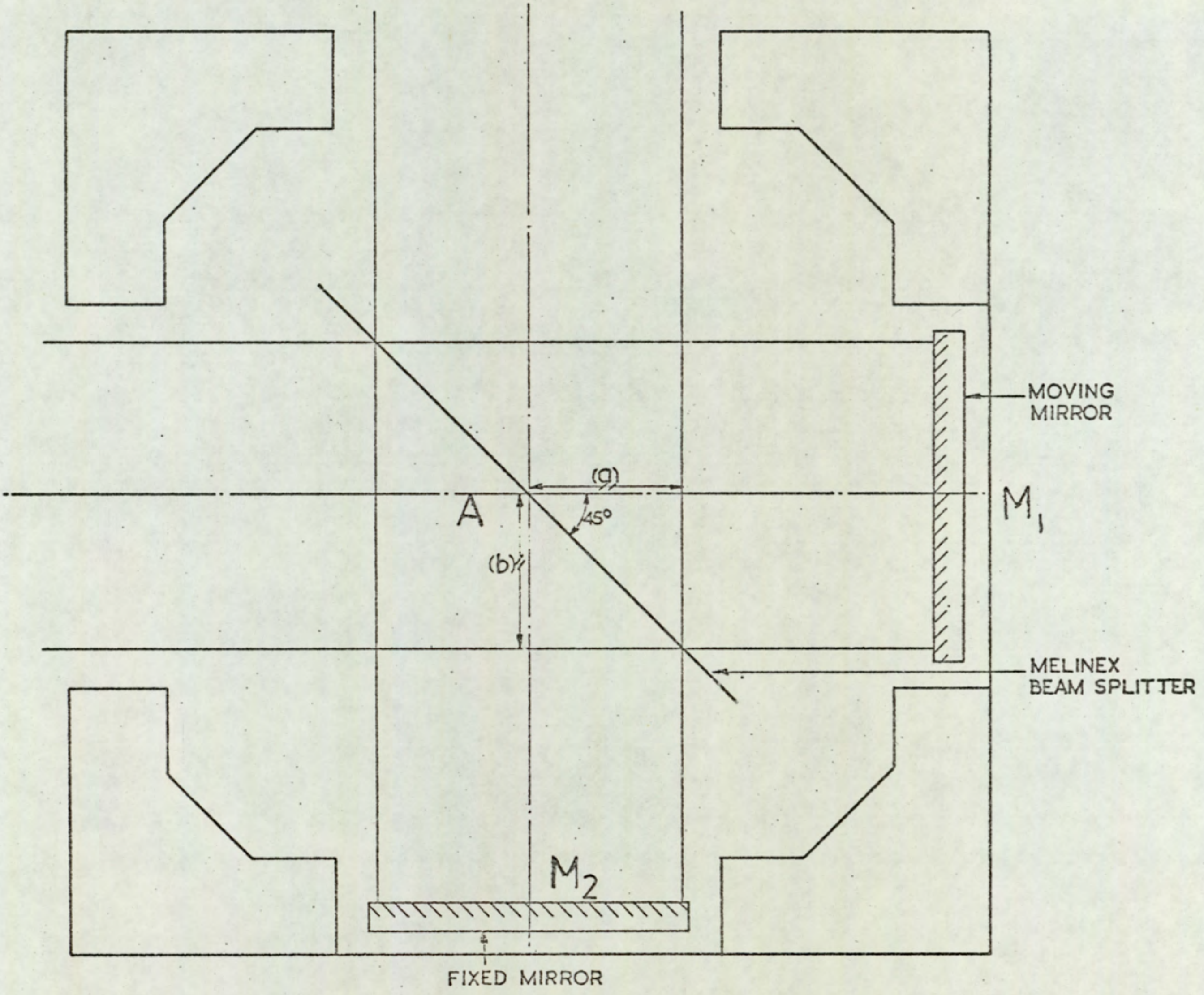


FIG. 2-2 BEAM SPLITTER MODULE

Industrial Instruments Company (R.I.I.C.) Fourier spectrophotometer is shown in the figure 2.1. The entire optical system is enclosed and evacuated to a pressure,less than 0.05 torr (1 torr is approximately equal to 1mm of Hg) in order to prevent atmospheric water vapour absorption. The source is a quartz jacketed, high pressure mercury lamp which is water cooled and has been shown to be better at lower frequencies than a heated global source.

The light energy from the lamp passes through a variable aperture . The light is now chopped by a three bladed chopper at a frequency of 15Hz. The chopper also activates a Reed switch, which produces a square wave output. The light energy is collimated and reflected by an off axis parabolic mirror (a). The collimated beam of light energy now strikes the melinex film (b) (which acts as a beam splitter) at an angle of 45^0, where half of the light is transmitted onto a fixed plane mirror (c) and the other half is reflected onto the moving mirror (d). The two beams of light are now both reflected and are recombined at the beam splitter. The radiation which is recombined after reflection by the mirror has certain frequencies which constructively interfere and others which destructively interfere. The interference arises because of the difference in the optical paths AM_1A and AM_2A shown in figure 2.2. This difference is continuously changed by a moving mirror M_1 at a constant rate but usually slow enough to average the noise to an acceptable value. The mirror is mounted onto a shaft which is moved toward and through the zero path difference i.e. where $AM_1A = AM_2A$.

The recombined beam of light is now condensed by an off axis parabolic mirror (e) onto a plane mirror (f) which directs the light to an intermediate focus (g). The sample is normally placed at the intermediate focus and if it is not positioned correctly the detector signal can be affected by 1-2% of its maximum value. The light now falls onto the black polythene fieldlens (h), and light core (i) where it is further condensed to reduce the size of the beam to 3mm, which is the size of the detector window. The detector window is transparent up to 625cm^{-1} but quartz can be used if the instrument is being used below 190cm^{-1}. The higher frequencies, i.e. those greater than 625cm^{-1} are filtered out by the black polythene.

The rays pass through the sample and filtering windows and are focused by another condensing system onto a Golay detector. The signal from the Golay is amplified and demodulated and the interferogram traced on a chart recorder, simultaneously the Golay signals are digitized at that particular point of mirror movement as determined by a Moire fringe system 200, and the digitized signals are recorded on paper tape, which serves as the input to a computer. The computerwith the help of a Fourier.2 program transforms the data and traces the spectrum.

There is no monochromator anywhere in the instrument and the radiation of the many frequencies passes through the sample but only those frequencies which are not selectively absorbed reach the detector. Because many frequencies are incident on the detector instead of just one, as is the case with grating spectroscopy, the signal to noise ratio is very large and this feature is known as the multiplex advantage in Fourier spectrometers.

The instrument is set up to operate in the region 40cm^{-1} to 400cm^{-1}. Most of the samples were run as nujol mulls using polythene supports. Only few spectra were run of solutions using either acetone or benzene as a solvent.

Nujol mulls were prepared as described earlier and placed on the polythene windows and the windows were put into a screw tight vacuum cell.

The operation of the instrument required great care. As the lamp has a thermocouple to keep the temperature of the socket low, so water was passed through the socket all the time during running of the instrument. First the water tap was opened to pass sufficient water through the socket. The main switch of the FS200 consul was switched on and then the chopper and finally the mecury lamp. Before running any sample, the FS200 electronic system should be warmed for at least one hour. To save time, sample cell was put into the sample chamber and the lid was replaced and tightened up. The instrument was evacuated to better than 0.05 torr to avoid water vapour absorption. A liquid nitrogen cold trap was used to get a better vacuum. After one hour the vacuum reached 0.05 torr.

For the region 40cm^{-1} to 400cm^{-1} the instrument was run at 2cm^{-1} resolution, and so it was run for 1000 digital counter unit. The digital counter was adjusted at 956 (i.e. 51 units from the zero path at 1007) by using speed 1000. The speed was adjusted at 10 for an actual run. The drive switch was switched on and also the recorder Telsec 700, and the gain on FS200 electronic was adjusted in such a way that the whole instrument was run at half load, i.e. only the 2" neon light on FS200 was lit up and all from 2^5 to 2^{10} neon lights were off. The recorder will show the pen at 50 deflection on a chart paper. The drive switched off and again the digital counter was adjusted at 956 unit using speed 1000 Now the punching machine was switched on and about 6" tape run and again switched off. The speed was adjusted to 10 and the drive was switched on to R (Raise) position. First two or three flashes were allowed to pass and then the punching machine was switched on just after the neon lights lit up otherwise incorrect data will be punched on the paper tape. The drive switch of the recorder was also switched on and the chart paper was allowed to run 1cm per minute to record the interferogram. The punching machine punched the amplified interferogram at constant time intervals on a paper tape. When the digital counter reached 1007 (i.e. zero free path, $AM_1A = AM_2A$ in fig 2.2) the recorder pen showed maximum deflection. The instrument was run until 1058 unit on digital counter and the drive was switched off. The punching machine also stopped and again about 6" of tape was allowed to run and then it was switched off. The vacuum was released and the sample was removed and replaced by another sample, and the whole operation was repeated for each sample. The spectra were computed by ICL 1905 computer at the University computer centre.

All the spectra were run twice, first with a thick mull and then with a thin mull. The instrument was calibrated with water vapour and the values of peaks were found to agree within $\mp$ 1 or 2 cm^{-1} with the expected values. Both the spectra of the same sample were found to be indentical except for the peak intensity. Also the spectra were compared with P.E.225 far infra-red instrument in the region of $200cm^{-1}$ to $400cm^{-1}$ and it was found that spectra of the same samples were reproduced in the Fourier spectrophotometer.

Raman Spectra

Most of the Raman spectra were recorded on the Cary 81 Raman spectrophotometer at the University of Nottingham using $6328A^0$ He - Ne laser exitation and on the Coderg PH1 Raman spectrophotometer at the University of Leicester using 6328A^o He - Ne laser exitation. On Cary 81 spectrmeter samples were examined by placing compounds in a glass sample bottle in a sample chamber. A little glycerine was used between the sample bottle and the entrance slit of the laser beam to avoid any laser scattering. Also in few cases solid samples were examined on a special sample rod with a little hole at the end of the rod in which a ground sample was placed. The sample holder was adjusted in such a way that a maximum deflection was observed on the chart paper. On the Coderg PH1 spectrometer solids were examined as samples weighing between 5 and 10mg. in a glass capillary tubes. Some spectra were obtained direct from the sample bottles. The best spectra were obtained from the cystalline solids.

Nuclear Magnetic Resonance Spectroscopy

^{1}H nuclear magnetic resonance (n.m.r.) spectra at 100MHz were recorded on the Perkin Elmer R14 spectrophotometer. For the thallium (I) systems dimethyl sulphoxide was used as a solvent with TMS used as an internal reference. A high concentration of sample was required and 4M solutions were used where possible. For the thallium (III) halide complexes both dimethyl sulphoxide and acetonitrile were used as the solvent. For the organotellurium compounds chloroform was used as a solvent. An attempt was made to measure ^{19}F n.m.r. signal but the compounds di(perfluorophenyl) tellurium dihalides were not sufficiently soluble to give the n.m.r. signals.

Mass Spectra

Mass spectra were recorded at 70eV with an AE1 MS9 mass spectrometer.

Conductivity Measurements

Molar conductivities were measured at room temperature with a mullard conductivity bridge and also with a Henelec MRA-38 conductivity bridge using 10^{-3} molar solutions. Both acetonitrile and nitromethane were used as a solvent.

Diffuse Reflectance Spectra

Diffuse reflectance spectra were recorded on the S.P.700 and the S.P.800 using the S.P.735 attachment with magnesium oxide used as a diluting agent. Two spectra were very kindly run by I. I. Bhayat.

X-Ray Powder Photographs

X-Ray powder photographs were taken using Cu - K_α radiation.

Analytical Measurements

The carbon, hydrogen and nitrogen analysis were done at the Reading University, and on the departments own machine. Few samples were sent to Dr. Strauss, Microanalytical Laboratory, Oxford and to Alfred Bernhardt, Microanalytical Laboratory, West Germany.

(b) PREPARATIONS OF COMPLEXES

Chemicals - All chemicals were obtained from the commercial sources and "Analar" grades were used whenever possible. Metal perchlorates were synthesised in the laboratory. Tri-(2-pyridyl)amine was prepared by the method of Wibaut and LaBastide[33].

Solvents - All the solvents were obtained from the commercial sources and were purified by literature methods, i.e. nitromethane[34], dimethylformamide[35], acetone[36a] and acetonitrile[36b].

Preparation of tri-(2-pyridyl)amine - This compound was prepared by the method of Wibaut and LaBastide[33]. The yield of the product depends on the quantity of the catalyst used[37]. In an ideal experiment, di-(2-pyridyl) amine (5.5gms) and 2-bromopyridine (5.2gms) were refluxed in mesitylene for 16 hours in the presence of potassium iodide (trace), copper bronze (2gms) and anhydrous potassium carbonate (6gms). The mesitylene and the excess 2-bromopyridine were removed by steam distillation and the residue extracted four times with boiling water (100ml). The resulting solid was recrystallised from water to M.P.131°C (lit M.P.130°C) yield 6.2grms (about 80%m lit.50%)

Found - C, 72.3; H, 4.7; N,22.3, calculated for $C_{15}H_{12}N_4$: C, 72.5; H,4.9; N,22.6

Preparation of 2,2'-bipyridyltrichlorothallium (III) - Preparation of thallic chloride in an aqueous solution has been known for many years. But thallic chloride prepared in this way was found to be prone to hydrolysis. So thallic chloride was prepared in a non-aqueous solvent[11]. Thallous chloride (1.2gm) was suspended in acetonitrile (30ml.) and chlorine gas was bubbled through the suspension until all the thallous chloride disappeared leaving a light yellow solution. The excess of chlorine gas was removed on warming on a waterbath to give the colourless thallic chloride solution. To this warm solution 2,2'-bipyridyl (0.8gm) in acetonitrile (10ml) was added. A white crystalline product came out on cooling. The crystals were filtered, washed with a little acetonitrile and finally with ether and dried in a vacuum desiccator - yield 1.65gm. The compound was recrystallized from ethanol. Found : C, 25.4; H, 1.7; N,6.0 calculated for $C_{10}H_8Cl_3N_2Tl$ C, 25.65; H,1.7; N, 6.00 %

Preparation of 2,2'-bipyridyltribromothallium (III) - Thallic bromide was first prepared by suspending thallous bromide (1.4gm) in acetonitrile (20ml) and bromine (0.8gm) was added dropwise with constant stirring until all the solid thallous bromide has been oxidized to thallic bromide. The excess of bromine was then boiled off leaving a colourless solution. To this warm solution 2-2'bipyridyl (o.80gm) in acetonitrile (20ml) was added. Light yellow crystals came down on cooling. The crystals were filtered, washed with acetonitrile and then with ether and dried in a vacuum desiccator .The compound was insoluble in alcohol, benzene and acetone so recrystallization was not possible. Yield - 2.7gms. Found: C, 20.5; H, 1.3; N,4.3 calculated for $C_{10}H_8Br_3N_2Tl$. C, 20.3; H, 1.3; N, 4.7%.

Preparation of 1,10-phenanthrolinetrichloro thallium (III) - Thallic chloride was prepared as above method from thallous chloride (1.2gm). To the warm colourless solution 1.10 phenanthroline monohydrate (0.95gm) in acetonitrile (20ml) was added. A white solid came out on cooling. The solidwas filtered, washed with acetonitrile, then with alcohol and finally with ether, and dried in a vacuum desiccator- yield 1.9gm. The compound was insoluble in a normal solvent such as benzene, acetone, alcohol etc. Found : C, 29.5; H, 1.8; N,5.6 calculated for $C_{12}H_8Cl_3N_2Tl$, C, 29.4;

H,1.6; N,5.7%.

Preparation of 1,10-phenanthrolinetribromothallium (III) - Thallic bromide was prepared as before from thallous bromide (1.4gm) in acetonitrile (30ml). To the warm solution 1.10 phenanthroline monohydrate (0.95gm) in acetonitrile (10ml) was added, immediately a white solid was formed. The solid was filtered, washed with acetonitrile, then with alcohol and finally with ether, and dried in a vacuum desiccator- yield 2.6gms. Found : C,23.1; H, 1.9; N, 4.9 calculated for $C_{12}H_8Br_3N_2Tl$. C,23.0; H, 1.3; N, 4.5%.

Preparation of di-(2-pyridyl)aminetrichlorothallium (III) - The preparation of this compound is known[13]. Thallic chloride was prepared as before from thallous chloride (1.2gms) in acetonitrile (30ml). To the cold solution di(2-pyridyl)amine (0.855 gm) in acetonitirle (20ml) was added. After standing for a few minutes a light yellow solid was formed. The solid was filtered, washed with acetonitrile and then with ether and dried in a vacuum desiccator- yield 2.2gm. Found : C, 24.6; H, 1.9; N, 8.9; calculated for $C_{10}H_9Cl_3N_3Tl$. C, 24.9; H,1.9; N,8.7%.

Preparation of di-(2-pyridyl)aminetribromothallium (III) - The preparation of this compound is not reported in the literature. Thallic bromide was prepared as before from thallous bromide (1.4gm) in acetonitrile (20ml). To the cold thallic bromide solution di-(2-pyridyl)amine (0.855gm) in acetonitrile (20ml) was added and the solution was stirred for ten minutes, when a light yellow solid was formed. The solid was filtered, washed with acetonitrile and then with ether and dried in a vacuum desiccator- yield 2.35 gms. Found : C, 18.18; H, 1.64; N,6.88, calculated for $C_{10}H_9Br_3N_3Tl$, C, 19.51; H, 1.397; N, 6.82%.

Preparation of tri-(2-pyridyl)aminetrichlorothallium (III) - Thallic chloride was prepared as before from thallous chloride (1.2gm) in acetonitrile (20ml). To the cold solution tri-(2-pyridyl)amine (1.21gm) in alcohol (20ml) was added. A white solid was formed on stirring. Some solvent was removed by evaporation, and the solid was filtered after cooling, washed with acetonitrile and then with ether, and dried in a vacuum desiccator- yield 2.56gm. Found : C,32.6; H, 2.3; N, 10.5, calculated for $C_{15}H_{12}Cl_3N_4Tl$ C, 32.2; H, 2.1; N, 10.0 %

Preparation of tri-(2-pyridyl)aminetribromothallium (III) - Thallic bromide was prepared as before from thallous bromide (1.4gm) in acetonitrile (20ml). To the cold solution tri-(2-pyridyl)amine (1.21gm) in acetonitrile (20ml) was added. Very light yellow crystals were deposited after evaporation of some solvent. The crystals were filtered, washed with a little acetonitrile and dried in a vacuum desiccator The compound was recrystallized from the ethanol and acetone mixture - yield 2.65gm. Found - C,25.0; H, 1.9 N, 8.0, calculated for $C_{15}H_{12}Br_3N_4Tl$ C, 26.0; H, 1.7; N, 8.1%.

Preparation of complexes with Dimethyl formamide (D.M.F.)

Preparation of Tl(bipy)D.M.F.Cl_3 - Tl(bipy)Cl_3 (0.5gm) was added to a small amount of pure dry dimethyl formamide. The mixture was warmed until the complex dissolved. The clear solution was then cooled in an ice bath when a fine white crystalline product was separated. The complex was washed with ethanol, then with diethyl ether and dried in a vacuum desiccator. Infra-red spectrum shows ν(CO) frequency at 1640cm^{-1}, (pure DMF gives ν(CO) band at 1678cm^{-1}). Found : C,29.0; H, 1.8; N, 8.0, calculated for $C_{13}H_{15}Cl_3N_3OTl$ C, 29.0; H, 2.8; N, 7.8%.

Preparation of Tl(bipy)D.M.F. Br_3 - Tl(bipy)Br_3 (0.6gm) was added to a small amount of pure dry dimethyl formamide. The mixture was warmed until the complex dissolved. The clear solution was then cooled in an ice bath but no crystals were formed. On addition of dry diethyl ether (3ml) slightly yellow solid was formed. The solid was filtered, washed with a little alcohol and then with diethyl ether and dried in a vacuum desiccator. The ν(CO) frequency was found at $1642cm^{-1}$.
Found : C,20.5; H, 1.6; N,6.0, calculated for $C_{13}H_{15}Br_3N_3OTl$ C,23.0; H, 2.2; N, 6.2 %.

Preparation of Tl(phen) D.M.F.Cl_3 - Tl(phen)Cl_3 (0.5gm) was added to a small amount of dimethyl formamide and the solution was warmed until the complex dissolved. On cooling in an ice bath, white crystalline product was separated. The crystals were filtered, washed with ethanol, then with diethyl ether and dried in a vacuum desiccator. The ν(CO) frequency was found at $1630cm^{-1}$. Found : C, 30.8; H, 2.6; N, 7.5, calculated for $C_{15}H_{15}Cl_3N_3OTl$ C,31.9; H, 2.6; N, 7.4 %.

Preparation of Tl(phen)D.M.F.Br_3- Tl(phen)Br_3 (0.5gm) was added to a small amount of pure dry dimethyl formamide and the mixture was warmed until the complex dissolved. On cooling the solution in an ice bath, a fine crystalline produce separated. The crystals were filtered, washed with alcohol, then with diethyl ether and dried in a vacuum desiccator . The ν(CO) frequency was found at $1632cm^{-1}$. Found : C, 25.8; H, 2.5; N, 5.7 calculated for $C_{15}H_{15}N_3OTl$ C, 25.8; H, 2.2; N, 6.0 %.

Preparation of Tl(dipyam)D.M.F. Cl_3 - Tl(dipyam)Cl_3 (0.5gm) was added to a small amount of pure, dry dimethyl formamide and the mixture was warmed until the complex dissolved. On cooling,the solution in an ice bath, a finecrystalline product separated. The crystals were filtered washed with alcohol, then with diethyl ether and dried in a vacuum desiccator. The ν(CO) frequency was found at 1650cm^{-1}.
Found : C, 27.7; H, 2.7; N, 10.1, calculated for $C_{13}H_{16}Cl_3N_4OTl$,
C, 28.1; H, 2.8; N, 10.1%

Preparation of Tl(tripyam)D.M.F.Cl_3 - Tl(tripyam)Cl_3 (0.5gm) was added to a small amount of pure, dry dimethyl formamide and the mixture was warmed until the complex dissolved. On cooling,the solution on an ice bath, a fine crystalline product separated. The white crystals were filtered, washed with alcohol, then with diethyl ether and dried in a vacuum desiccator. Teh (CO) frequency was found at 1640cm^{-1}.
Found : C, 34.2; H, 3.2; N, 11.1, calculated for $C_{18}H_{19}Br_3N_5OTl$ C, 34.2; H, 3.0; N, 11.1 %.

Preparation of bis(1,10phenanthroline)thallium (I) perchlorate - Thallous perchlorate (0.3gm) was dissolved in water (15ml). In another beaker 1,10 phenanthroline mono hydrate (0.39gm) was dissolved in absolute alcohol (10ml). The two solutions were mixed and stirred, when a white solid was formed. The solid was filtered, washed with dilute alcohol, then with a little absolute alcohol and dried in a vacuum desiccator- yield 0.563gm . The complex was recrystallized from hot absolute alcohol - yield .49gm
Found : C, 43.4; H, 2.4; N, 8.5, calculated for $C_{24}H_{16}ClN_4O_4Tl$ C, 43.4; H, 2.4; N, 8.4 %.

Preparation of bis(1,10-phenanthroline)thallium (I) nitrate - Thallous nitrate (0.26gm) was dissolved in water (10ml), in another beaker 1-10 phenanthroline hydrate (0.39gm) was dissolved in absolute alcohol (10ml). The two solutions were mixed and stirred when a white solid was formed. The solid was filtered, washed with aqueous alcohol and then with absolute alcohol, and dried in a vacuum desiccator- yield 0.5gm). The complex was recrystallised from hot absolute alcohol. Found : C,44.7; H, 2.2; N,10.7 calculated for $C_{24}H_{16}N_5O_3Tl$ C, 46.0; H,2.6; N, 11.2 %.

Preparation of bis(2,2'-bipyridyl)thallium (I) perchlorate - Thallous perchlorate (0.3gm) was dissolved in a hot acetone (75ml) with constant stirring. Some thallous perchlorate was left as insoluble residue. In another beaker 2,2'-bipyridyl (0.5) was dissolved in acetone (20ml) and added to the hot solution of $TlClO_4$. On adding bipyridyl solution undissolved $TlClO_4$ residue was dissolved and a clear solution was formed. The solution was concentrated to about 40ml and left for crystallisation. A fine colourless crystal was obtained, filtered and dried in a desiccator During the preparation of this compound excess of bipyridyl was needed to dissolve all $TlClO_4$. The compound was susceptible to hydrolysis yield 0.45gm . Found : C, 39.1; H, 2.6; N, 9.4 calculated for $C_{20}H_{16}ClN_4O_4Tl$ C, 39.7; H, 2.6; N, 9.1 %.

Attempts were made to prepare $Tl(bipy)_2NO_3$ but were unsuccessful because thallous nitrate was not soluble in acetone and water decomposed the complex. Attempts were also made to prepared thallium (I) complexes with other nitrogen donor ligands such as di-(2-pyridyl)amine, tri-(2-pyridyl) amine etc., but in all attempts no complex formation was observed and every time the thallium (I) salt and the free ligands were isolated.

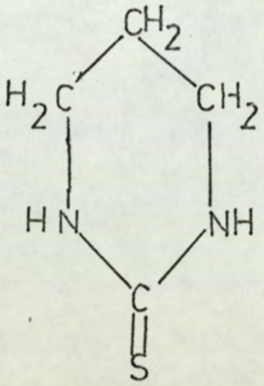
The reaction between bis (2,2'-bipyridyl)-thallium (I) perchlorate and borontrifluoride:-

Bis (2,2'-bipyridyl)thallium (I) perchlorate (0.6gm) was dissolved in a dry diethyl ether (100ml) under nitrogen atmosphere in a dry box. To this solution boron trifluoride in ether (about 1ml, 20% w.w) was added and the content was refluxed for one hour in the dry box. After one hour all the solvent was removed and the residue was collected. The infra-red spectrum of the above compound did not show any of bipyridyl group vibration and the spectrum was simple with a very broad absorption in the region 1400 to 800 cm^{-1}. The analytical data of the above compound was obtained as follows: Found - C,24.57; H,2.07; N,5.83 calculated for $C_{20}H_{16}BClF_3N_4O_4Tl$ C, 35.11; H,2.508; N, 8.19%.

Both the results indicate that the desired product $[Tl(bipy)_2.BF_3]ClO_4$ was not formed. Similar results were obtained when $Tl(bipy)_2ClO_4$ was treated with another Lewis acid antimonypentachloride.

Preparations of the complexes of Thallium (I) with sulphur donor ligands

Preparation of Hexahydropyrimidine - 2-thione - The compound was prepared as described by McKay and Holton[38]. In a 500ml. three necked round bottomed flask absolute alcohol (15ml) and 2 pallets of KOH was taken. When the KOH had been dissolved, carbon disulphide (CS_2) (200ml) was added.A large efficient condenser was placed in one neck of the flask and in the other neck a separating funnel containing 1:3 diamino propane (30ml) was placed.



The amine was added very carefully as the reaction is violent, and so only 0.5ml. amine was added at a time.

During the addition a white solid product was formed. After the addition of all amine the excess of carbon disulphide was distilled off on a water bath using all precautions of an ether distillation.

The white solid was removed from the flask by dissolving it in warm water (approximately 200ml). Recrystallisation was carried out until it was completely free from hydrogen sulphide. The white needle shape crystals were analysed. Found : C, 39.97; H, 7.26; N, 24.7 calculated for $C_4H_8N_2S$ C, 41.37; H, 6.89; N, 24.14.%

Preparation of tetrakis (thiourea)thallium (I) nitrate - Thallous nitrate (0.266gm) was dissolved in warm water (10ml). In another beaker thiourea(0.34gm) was also dissolved in warm water. The two warmed solutions were mixed and cooled slowly at room temperature. After some time white needle shaped crystals were formed. The crystals were filtered, washed with a little cold water and dried in a vacuum desiccator

When the mixed solution was cooled rapidly (i.e. in an ice bath) the crystals were found to be light yellow in colour. Also when the white crystals were heated in a test tube over 60^{o}C in a water bath, the crystals were turned to light yellow, but on cooling slowly again white crystals were obtained. Found : C, 6.16; H, 2.58; N, 20.72; S, 20.98 calculated for $C_4H_{16}N_9O_3S_4Tl$, C, 6.68; H, 2.8)5; N, 22.09; S, 22.44%

Preparation of tetrakis (thiourea)thallium (I) perchlorate - Thallous perchlorate (0.3gm) was dissolved in water (10ml) and heated to 60^{o}C, also thiourea (0.34gm) was dissolved in water (10ml) and heated to 60^{o}C. The two warmed solutions were miexed and cooled very slowly at room temperature. On cooling white, needle shaped crystals were formed. The crystals were filtered, washed with a little cold water and dried in a vacuum desiccator. Found : C, 8.05; H, 2.61; N, 18.31; S, 21.36 calculated for $C_4H_{16}ClN_8O_4S_4Tl$, C, 7.9; H, 2.63 ; N, 18.42; S, 21.36%.

Preparation of tetrakis (thiourea)thallium (I) thiocyanate - Thallous thiocyanate (0.272gm) was dissolved in warm water (30ml). In another beaker thiourea (0.34gm) was dissolved in water (10ml). The two warm solutions were mixed and heated for five minutes. The hot solution was filtered and allowed to cool at room temperature. On cooling slowly white shining crystals were formed which were filtered, washed with a little cold water and dried in a vacuum desiccator. Found : C, 10.1; H, 2.57; N, 18.82 calculated for $C_5H_{16}N_9S_5Tl$, C, 10.43; H, 2.71; N, 19.43 %.

Preparation of octakis (thiourea)dithallium (I) sulphate - Thallous sulphate (0.5gm) was dissolved in water (20ml). In this particular preparation a little dilute sulphuric acid was added to make an acidic solution. In another beaker thiourea (0.6gm) was dissolved in water (25ml). Both the solutions were heated to 60°C and mixed. On cooling very slowly white needle shaped crystals were formed. The crystals were filtered, washed with a little water and dried in a vacuum desiccator. Found : C, 8.12; H, 2.75; N, 19.73, calculated for $C_8H_{32}N_{16}O_4S_9Tl_2$, C, 8.626; H, 2.875; N, 20.12 %.

Preparation of tetrakis (hexahydropyrimidine-2-thione) thallium(I) perchlorate - Thallous perchlorate (0.3gm) was dissolved in water (15ml) In another beaker hexahydropyrimidine-2-thione (0.464gm) was dissolved in water (15ml). Both the solutions were heated to 60°C and mixed. On cooling very slowly white needle shaped crystals were formed. The crystals were filtered, washed with a little water and dried in a vacuum desiccator. Found : C, 24.82; H, 4.2; N, 14.09; S, 17.04, calculated for $C_{16}H_{32}ClN_8O_4S_4Tl$, C, 24.68; H, 4.11; N, 14.4; S, 16.63%.

Preparation of tetrakis (hexahydropyrimidine-2-thione) thallium (I) nitrate - Thallous nitrate (0.266gm) was dissolved in water (10ml). In another beaker hexahydropyrimidine-2-thione (0.46gm) was dissolved in water (15ml). The two solutions were mixed and heated at 70°C with stirring. On cooling slowly white shining flake-like crystals were formed. The crystals were filtered and washed with water and dried in a vacuum desiccator. Found : C, 25.36; H, 4.18; N, 16.6; calculated for $C_{16}H_{32}N_9O_3S_4Tl$, C,26.29; H, 4.38; N, 17.26 %.

Attempts were made to prepare complexes of thallous sulphate and thallous thiocyanate with hexahydropyrimidine-2-thione, but no complex formation was observed. The infra-red spectra of the final product did not confirm the complex formation. All the analytical data of such a product was not satisfactory for the required formula.

CHAPTER 3 - RESULTS AND DISCUSSION

A. RESULTS

TABLE 1

Infra-red spectra (400-80cm^{-1}) of some thallium (III) complexes

Complexes	(TlX)	(TlX)	Other bands
$\mathrm{TlCl_3}$(bipy)	295(s), 278(s), 250(s) 233(s), 229(sh)	123(s), 110(s), 87(s)	362(m), 169(m), 153(m), 136(m)
$\mathrm{TlBr_3}$(bipy)	204(s), 198(s), 187(s) 181(sh)		281(m), 218(m), 162(m), 151(m)
$\mathrm{TlCl_3}$(bipy)-DMF	296(m), 284(s)m 265(s), 251(s), 232(m)		139 (m)
$\mathrm{TlBr_3}$(bipy)-DMF	199(s.b.),187(s)		356(w), 228(m), 217(m), 162(w.m.), 151(m),140(m)
$\mathrm{TlCl_3}$(phen)	295(s), 273(s), 260(s), 249(s)	120(s),104(sh), 97(s)	384(m),166(s)
$\mathrm{TlCl_3}$(phen) Raman shifts	292(s), 272(w), 256(w)	128(s), 104(s), 89(s)	
$\mathrm{TlBr_3}$(phen)	204(s), 190(s), 170(s), 159(s)		383(m), 287(m), 240(m), 107(m)
$\mathrm{TlCl_3}$(phen)-DMF	282(s), 263(m), 254(s)	118(m),88(m)	385(s), 345(m), 295(sh), 170(m)
$\mathrm{TlBr_3}$(phen)-DMF	193(s), 180(s), 169(s)		360(m), 340(m), 240(w) 137(m), 104(w)
$\mathrm{TlBr_3}$(phen)-DMF Raman shifts	191(s), 183(s), 167(s)		296(w), 134(m), 109(m)
$\mathrm{TlCl_3}$(dipyam)	287(s), 266(s), 257(s), 240(s)	137(s), 116(s), 99(s)	389(w),373(w), 346(m), 340(sh), 205(w), 188(w)

Table 1 cont.

Complexes	(TlX)	(TlX)	Other bands
TlCl$_3$(dipyam)-DMF	279(s), 253(s), 243(s)	130(w), 115(s.b)	386(m), 372(m), 348(m), 336(m), 320(b).
TlCl$_3$(tripyam)-	302(s), 276(s), 252(s)	116-85(s) poor resolution	394(m), 374(m), 366(m), 224(m), 207(w), 160(m).
TlBr$_3$(tripyam)	207(s), 199(s), 193(s)		386(m), 374(m), 341(m), 244(m), 233(m), 181(s)
TlCl$_3$(tripyam)-DMF	277(s), 261(s), 250(s)	122(s), 116(s), 101(s)	383(m), 366(m), 355(m), 310(m), 211(m), 207(m), 134(s).
$[\mathrm{Tl(Phen)_2}](\mathrm{NO_3})$			249(m), 245(m), 239(m), 119(m)
$[\mathrm{Tl(Bipy)_2}](\mathrm{ClO_4})$			339(m), 186, 125(b)

TABLE 2

Conductivity measurements in approximately 10^{-3}M solutions

Compounds	Solvents		
	Dimethyl Formamide	Methyl Cyanide	Nitromethane
$TlCl_3$(bipy)DMF	32 $\mathrm{Ohm}^{-1}\mathrm{cm}^{2}\mathrm{Mole}^{-1}$		
$TlBr_3$(bipy)DMF	38 " " "		
$TlCl_3$(phen)DMF	26 " " "		
$TlCl_3$(dipyam)·DMF	31 " " "		
$TlCl_3$(tripyam)			
Freshly prepared soln.		65.28 $\mathrm{Ohm}^{-1}\mathrm{cm}^{2}\mathrm{Mole}^{-1}$	32.64 $\mathrm{Ohm}^{-1}\mathrm{cm}^{2}\mathrm{Mole}^{-1}$
After 24 hrs.		80.24 " " "	
$TlBr_3$(tripyam)			
Freshly prepared soln.		90.00 " " "	55.76 " " "
After 24 hrs.		100.6 " " "	

TABLE-2a

Infra-red and Raman spectra of thallium (I) complexes with sulphur ligands

	I.R.	Raman	I.R. (Tl-S)Raman
$TlClO_4(TU)_4$	995,168(s.b)	61 s, 99 s, 114 s	99 s
$TlNO_3(TU)_4$	110 s,165 s.b	125 m, 183 s,	110 s
$TlSCN(TU)_4$	98 s, 174 s	107 s,143 s,	98 s(i.r),107 s (R)
$Tl_2SO_4(TU)_8$	107 s,168 s.b,	67 s,108 s,183 s.	107 s(i.r),108 s(R)
$TlClO_4(HHPT)_4$	90 s,165 s.b,320 s.	153 s,180 s,325 w.	
$TlNO_3(HHPT)_4$	98 s,178 s.b,319 s.		98 s.
$TlSCN(HHPT)_4$	105 s,165 s.b,320 s.		105 s.

CHAPTER 3

B. DISCUSSION

Complexes of the type TlX_3L (where L = bipy, phen & dipyam) were prepared, all of which have been prepared previously by other workers with the object of elucidating their structure. McWhinnie[39] made the suggestion that the ionic structure for the above complexes could not be eliminated, and later he made the observation that the position of the thallium-chlorine stretching frequencies for $TlCl_3(bipy)$ could be compatible with the formulation.

$$Tl(bipy)_3^{3+}(Tl_2Cl_9)^{3-}$$

and explained the conductivity data by the dissociation

$$2 \ \left[Tl(bipy)_3\right]^{3+} \left[Tl_2Cl_9\right]^{3-} \rightleftarrows 3\ Tl(bipy)_2Cl_2^{\ +} + 3TlCl_4^{\ -}$$

Nord and Farver[39a] had prepared the complex $Tl(bipy)_3(ClO_4)_3$ and shown that in solution the above type of dissociation did in fact occur. On the other hand, as described in the introduction Walton suggested that the above complexes might have a non-centrosymmetric halogen bridged dimeric structure.

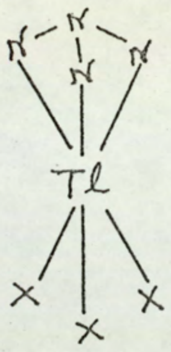
Hudman[40] reported the ultraviolet spectra of $TlCl_3(bipy)$, which showed a band at 282nm (35,500cm^{-1}), 238nm (42000cm^{-1}) and 210nm (49000cm^{-1}). These bands essentially correspond to $\pi - \pi^*$ transition in the ligands. The first bands occur in the free ligand at 35700cm^{-1} and 42550cm^{-1} respectively which on co-ordination to thallium experience a red shift i.e. to longer wave length. It has been noted for bipyridyl that when the charge on metal atom is +2 or greater, the first band to correspond

35500cm^{-1} is often split to the order at 1000cm^{-1} and also the red shift increases as the number of charges on the metal ion increases[40a]. However, for $TlCl_3$(bipy) the red shift is very small and there was no splitting of the band at all so the presence of $Tl(bipy)_3^{3+}$ in the solid state is very unlikely.

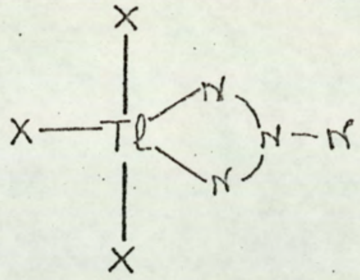
Further evidence of these species comes from the far infra-red spectra of $Cs_3Tl_2Cl_9$ which has been the subject of a normal co-ordinate analysis by Beattie[41]. His results showed the highest thallium-chlorine stretching mode to occur at 279cm^{-1}. However, as seen from the infra-red results for $TlCl_3$(bipy), $TlCl_3$(phen), $TlCl_3$(dipyam) (table-1), the thallium-chlorine stretching modes occur at higher frequencies around 300cm^{-1} than for $Cs_3Tl_2Cl_9$. In addition the position of the thallium-chlorine stretching vibrations do not correspond well with those of $Cs_3Tl_2Cl_9$, thus the ionic structure may be discounted for $TlCl_3$(bipy) and by analogy for TlX_3(Chelate).

The bromide and chloride thallium (III) complexes with tri-(2-pyridyl) amine (tripyam) have been prepared. The base can function as a terdentate ligand or as a bidentate ligand. The complexes were analysed stoichiometrically to $TlCl_3$(tripyam) and $TlBr_3$(tripyam). They were found to be non-electrolytes (neutral species) from the conductivity measurements in acetonitrile (table.2).

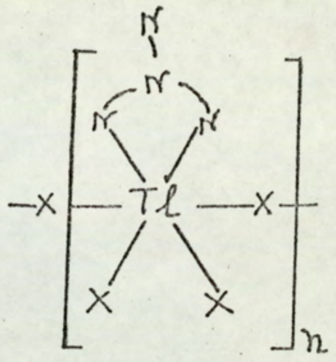
The infra-red spectra in the region 400-800cm^{-1} have been shown to be a useful guide to whether the tri-(2-pyridyl)amine is terdentate or bidentate. Essentially the spectrum is more complex for bidentate tri-(2-pyridyl) amine than for the terdentate tri-(2-pyridyl)amine in these regions. The ^1H n.m.r. spectrum of $TlBr_3$(tripyam) has been obtained since the complex was sufficiently soluble in acetonitrile for n.m.r. measurement.



3.1a



3.1b



3.1c

The three structures above illustrate the possible terdentate and bidentate tri-(2-pyridyl)amine cases. From the n.m.r. point of view all the three pyridyl rings are equivalent in structure (a), so they should produce a spectrum characteristic of a mono substituted pyridine.

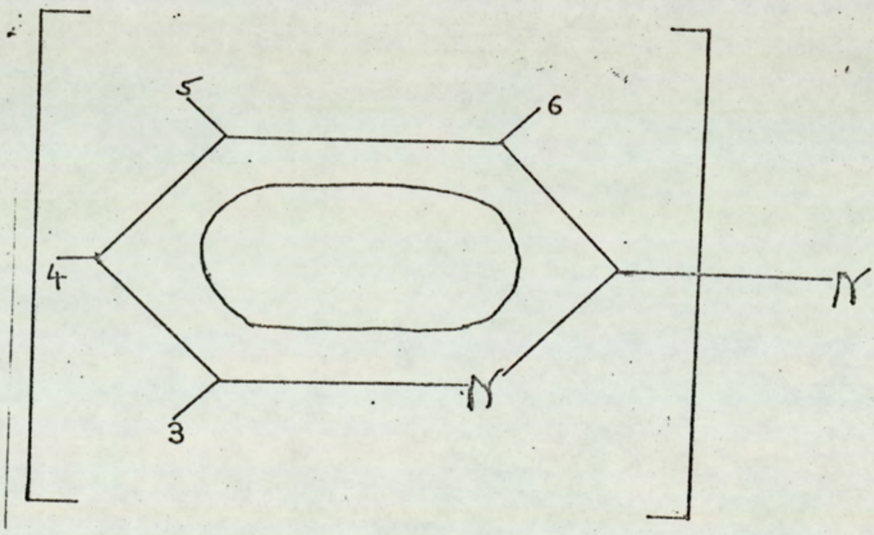
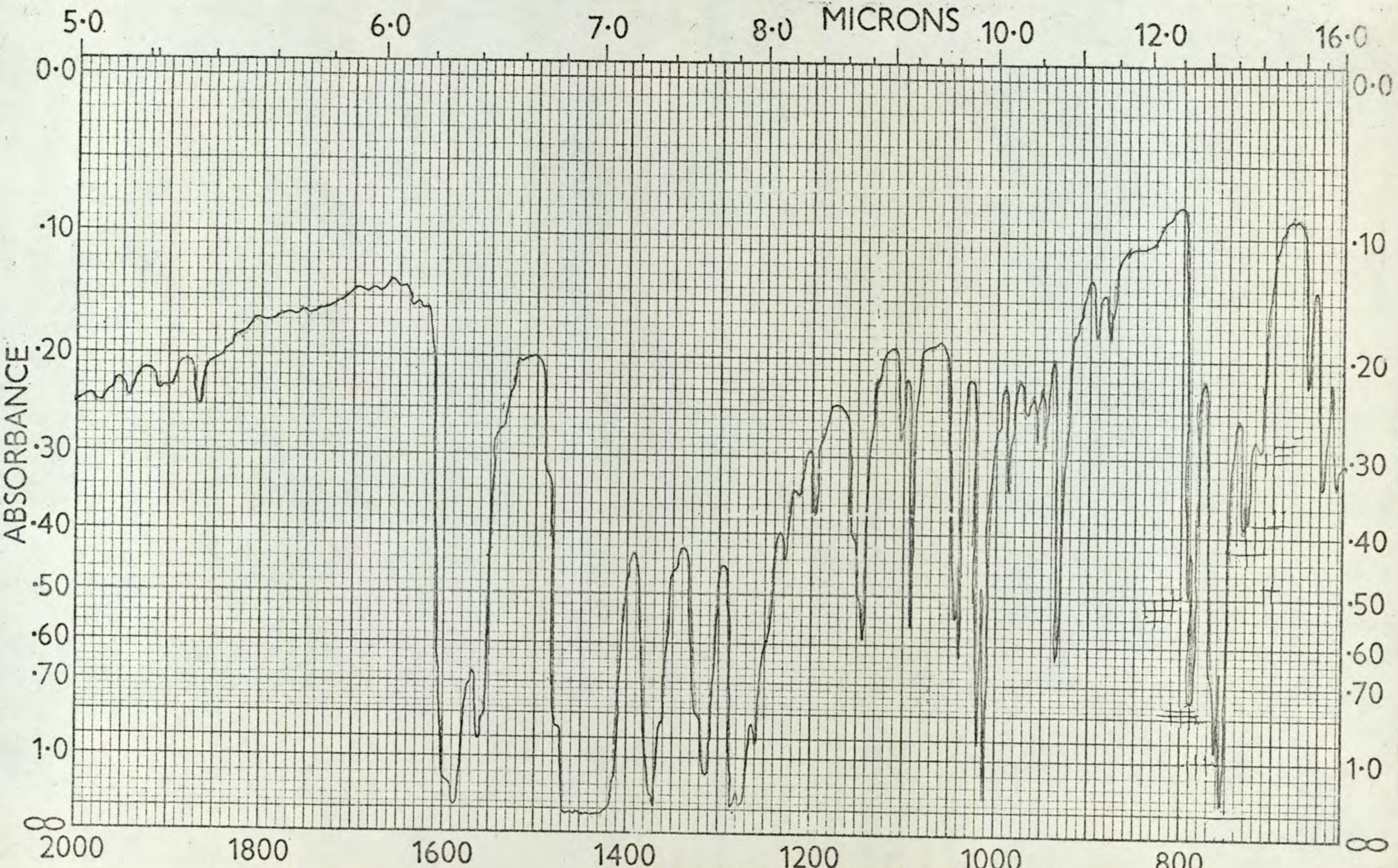


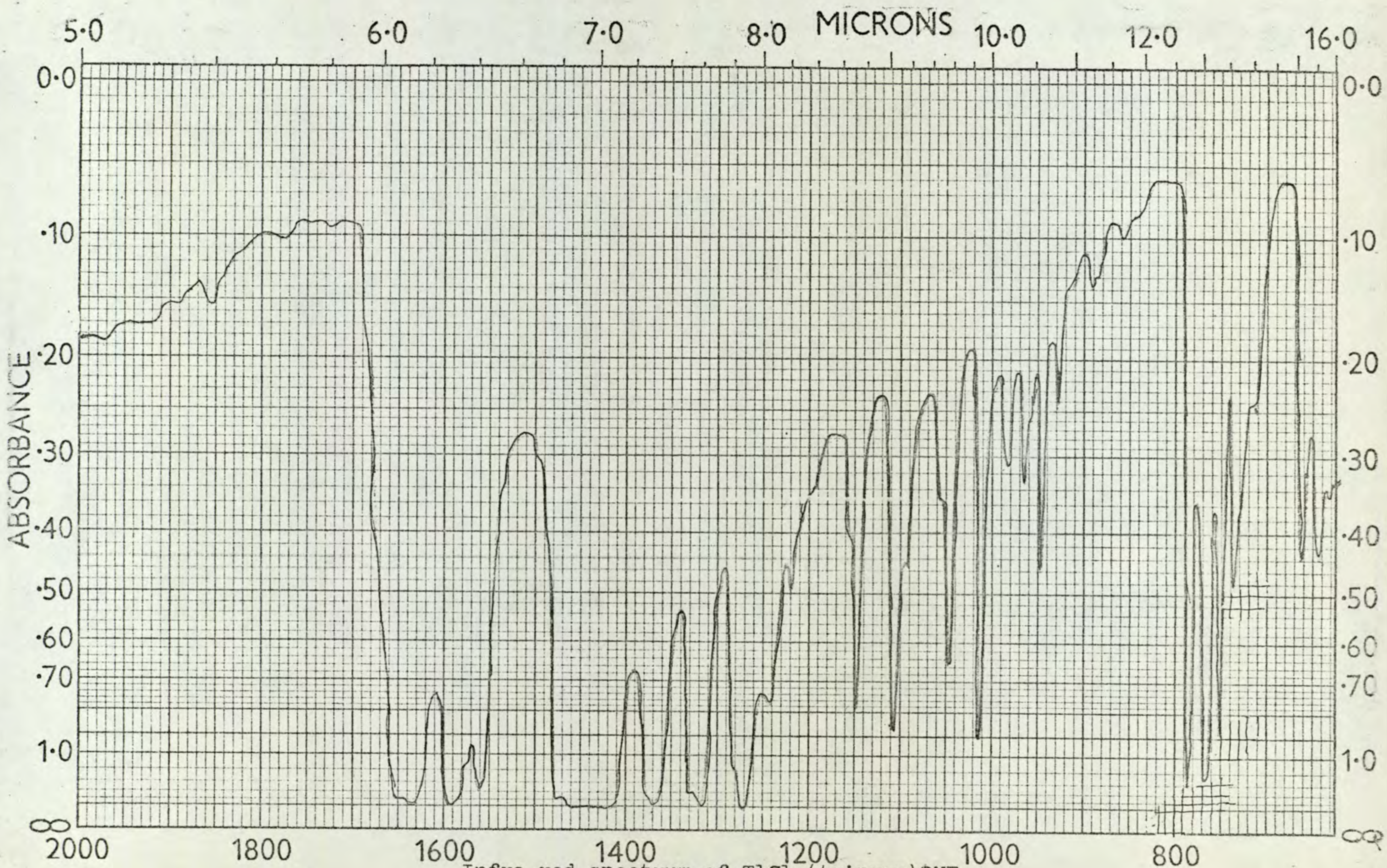
Fig.3.2

The protons in the pyridine ring are all nonequivalent and one should expect an approximation to an ABCD type spectrum. So there should be four main bands corresponding each nonequivalent proton in turn, each being doubly split doublet. The spectrum for the bidentate tri-(2-pyridyl) amine cases would be expected to be much more complex since the three pyridine rings are no longer equivalent and so the spectrum would be too complex to analyse completely. Hudman's spectrum in fact clearly consists of four main bands, each being a doubly split doublet, possibly split further in some cases, which was exactly what would be expected for terdentate strucutre. Hudman prepared the known $ZnCl_2$(tripyam) in which tri-(2-pyridyl)amine is known to be bidentate and the n.m.r. spectrum of the above complex was more complex and similar to free base i.e. tri-(2-pyridyl)amine. This suggests that the spectrum of $TlBr_3$(tripyam) supports the terdentate co-ordination tri-(2-pyridyl)amine in the complex.

The structure is even further supported by far infra-red spectra for both $TlCl_3$(tripyam) and $TlBr_3$(tripyam) which show basically three peaks corresponding to the terminal thallium-chlorine stretching frequencies. If the complex is considered to belong to point group C_{3v}, (molecular models indicates the local symmetry of terdentate tri-(2-pyridyl)amine is strictly C_{3v}) one would expect from symmetry considerations two infra-red active modes corresponding to Tl-Cl stretches $1A_1 + 1E_1$. However, the thallium chlorine stretching region is richer than anticipated for a complex of C_{3v} symmetry. The n.m.r. spectra support that the ligand is a terdentate in the complex and therefore the observation of three bands assignable as thallium chlorine stretching frequencies arise from the splitting of the degenerate E mode in C_{3v} symmetry by crystal field effects. It is now known that the $FeCl_3$(tripyam) also has a split E mode[41a]. The tri-(2-pyridyl)amine was terdentate in the complex with C_{3v} symmetry, and three infra-red active bands were observed.



Infra-red spectrum of $TlCl_3$(tripyam)



Infra-red spectrum of $TlCl_3$(tripyam) DMF.

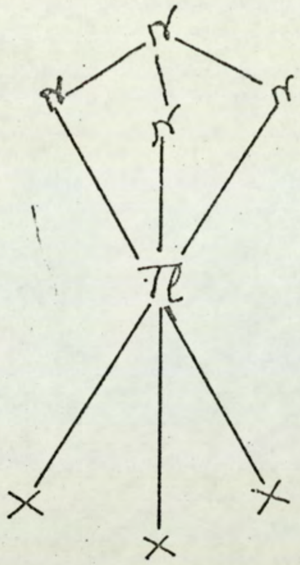


Fig. 3.3

When $TlCl_3$(tripyam) was recrystallized from dimethyl formamide (D.M.F.), a new white crystalline complex was obtained. The complex was analysed to the stoichiometric formula $TlCl_3$(tripyam)D.M.F. Evidence that the dimethyl formamide molecule is actually co-ordinated and not just solvent of crystallization, comes from the infra-red spectrum. The position of the carbonyl stretching frequency is observed at $1640cm^{-1}$ whereas the carbonyl stretch for the free dimethylformamide occurs at $1678cm^{-1}$. The complex has a terdentate tri-(2-pyridyl)amine base but on co-ordination of dimethyl formamide, one pyridine group is replaced by dimethyl formamide and the base can act as a bidentate ligand. The infra-red spectra of a typical bidentate tri-(2-pyridyl)amine is known[41b], but the spectra of the above complex was found to be more complex than for the terdentate tri-(2-pyridyl)amine in $TlCl_3$(tripyam). Also the far infra-red spectra of the above complex is very different than the

$TlCl_3$(tripyam) in the region of thallium-chlorine stretching frequencies. Also the stoichiometric formula and co-ordinate dimethylformamide shows that the complex would have a bidentate tri-(2-pyridyl)amine unless a co-ordination number higher than six is invoked for thallium.

Complexes of thallium (III) halides with a chelating ligands(chelate = bipy, phen, dipyam etc.)

When other TlX_3(chelate) was recrystallized from dimethylformamide (D.M.F) new crystalline complexes were found to be of the stoichiometric formula TlX_3(chelate)D.M.F. Also the ν(CO) band frequency was shifted to a lower wave number than the free dimethylformamide ν(CO) frequency. This result indicates that in all the dimethyformamide complexes D.M.F. was co-ordinated to thallium. All TlX_3(chelate)D.M.F. complexes have very similar infra-red spectra in ν(Tl-Cl) region which suggests that all the complexes have the similar structure. Two possible structure of the TlX_3(chelate)D.M.F. complexes are shown in the figure.

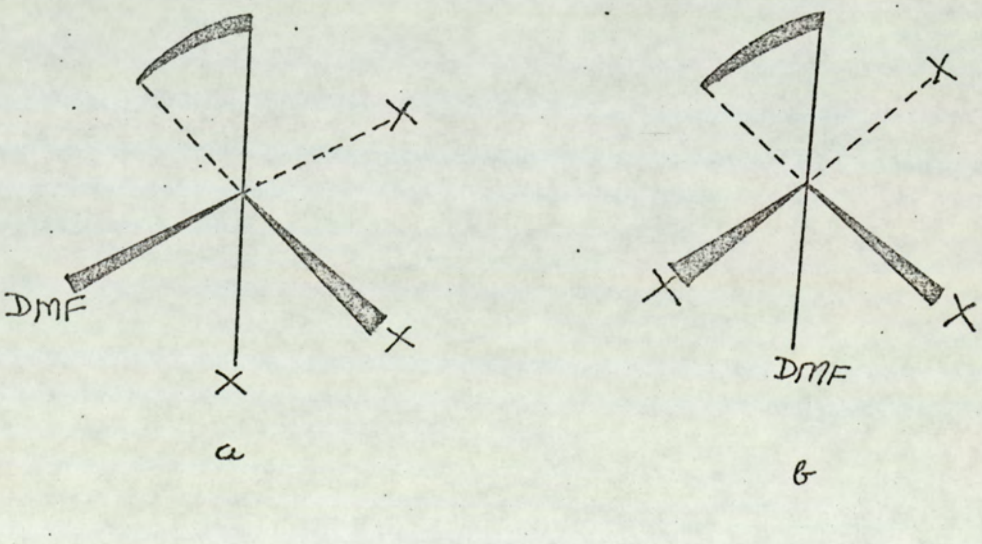


Fig 3.4

In the case of $TlCl_3$(Phen)DMF, it was possible to obtain a Raman spectrum. The coincidence of each infra-red and Raman bands below $400cm^{-1}$ indicates the low symmetry of the complex, thus the result is compatible with the structure 3-4a or 3-4b, If the local symmetry of the TlX_3 unit were to determine the spectrum in the ν(TlX) region, 3-4b would be favoured over 3-4a however, there is no justification for such arguments which depend only on the spectroscopic data and so only spectroscopic data would not help to determine the possible structure.

As described earlier, the terdentate tri-(2-pyridyl)amine may open out to become bidentate, another ligand entering the co-ordination sphere without disturbing the other ligands and maintaining the constant co-ordination number at the metal ion. Assuming no rearrangement of other ligands within the primary co-ordination sphere to occur during the reaction.

$TlCl_3$(tripyam) + D.M.F. $TlCl_3$(tripyam)DMF

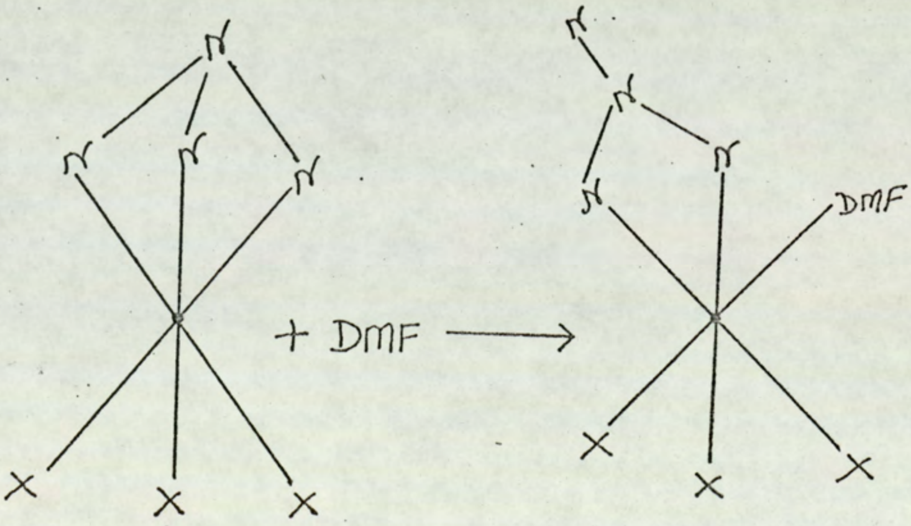
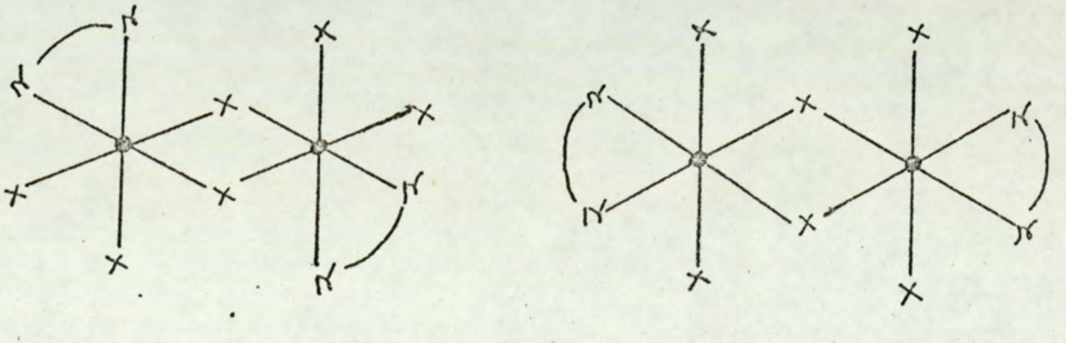


Fig. 3.5

The terdentate $TlCl_3$(tripyam) was confirmed by n.m.r. and infra-red spectroscopy. The possible structure of the above complex is shown in figure 3.3, then it would be possible to represent the reaction with dimethylformamide, when one of the pyridine group of tri-(2-pyridyl) amine open out from the terdentate co-ordination sphere to become bidentate. (fig.3.5).

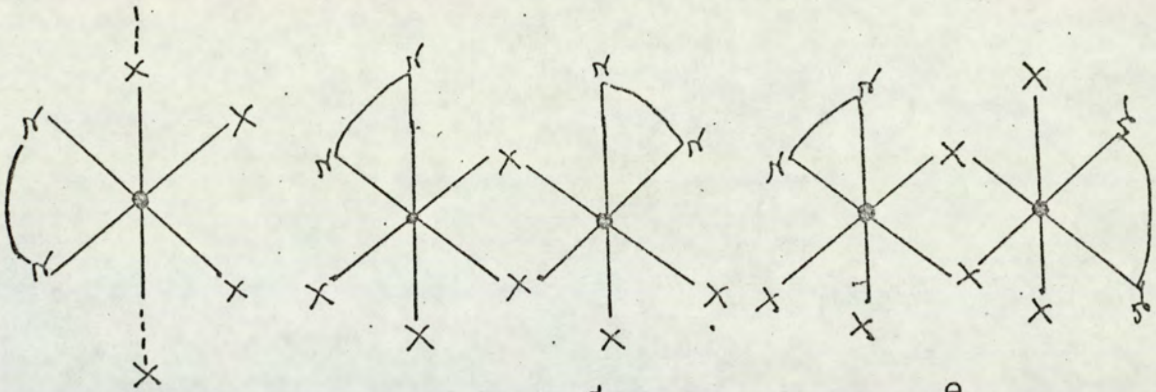
Due to the similarity of the infra-red spectra of all the TlX_3(chelate)DMF complexes, with the spectrum of $TlCl_3$(tripyam)DMF, it is believed that all the complexes would have the similar structures. An alternative view would be that the DMF adds to the complex to increase the co-ordination number at thallium, since the highest ν(Tl-Cl) frequencies shift downwards on complex formation. However, this shift merely reflects a lower effective positive charge for the thallium ion in the DMF complex which may equally well arise from the different ligand environments in the six co-ordinate species proposed above. Also the data for the tri-(2-pyridyl)amine complexes do not lend themselves to this interpretation and it is the similarity of the DMF complexes with $TlCl_3$(tripyam)DMF upon which the above arguments are based. It can be argued that the cis-TlX_3 configuration might also be characteristic of TlX_3(chelate), the DMF complexes probably arising by splitting of halogen bridges. So the above complexes can be represented as shown in the figure 3.6 below, some possible dimeric and one possible polymeric structure for TlX_3(chelate).



a

b

Fig. 3-6



C

d

e

Fig- 3-6

The (Tl-X) stretching bands have been assigned for all the complexes prepared, making use of the mass effect on substituting Br for Cl i.e. the ratio for TlBr/TlCl being approximately 0.7 and the metal halogen stretching bands are all very intense and broad.

The number of infra-red and Raman active stretching modes which would be expected for the Tl-X band can be calculated. For the first two structures using group theory, considering structure 3-6a, this belongs to the point group C_i i.e. it only has the centre of inversion and the identity as symmetry element. From the character table one can calculate the number of Raman and infra-red active band. In this particular case, the vibrational modes span the irreducible representations 4Ag + 4Au which are the fundamental modes. The 4Ag modes will be Raman active but infra-red inactive, whereas the 4Au modes will be infra-red active but Raman inactive. Therefore, there should be four bands in far infra-red corresponding to the 4Au stretching modes and four bands in the Raman spectra corresponding to the 4Ag stretching modes. Furthermore two of the four intra-red bands will correspond to terminal Tl-X stretches and two for the bridging Tl-X stretches, and it is also reasonable to suppose that the two bridging bands will occur at lower frequencies to the terminal bands.

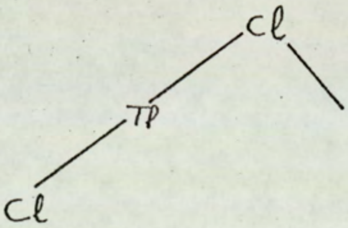
A similar analysis can be carried out for the structure 6b which belongs to the D_{2h} point group. Here also four infra-red active bands are predicted for this structure and since both structure 3.6a and 3.6b contain a centre of symmetry, there will be no co-incidences of the Raman and infra-red active bands. However from the results for $TlCl_3$(phen) the co-incidencies of the Raman and infra-red active bands could rule out the above two possible structures (table-I). Walton made a similar suggestion that all the chelate complexes would have the non-centrosymmetric structures.

It has been also calculated that the alternative polymeric structure 3.6c also predict four stretching modes to be active in the far infra-red. However, the solution of this problem may be afforded on consideration of the new complexes which analysed to the stoichiometric formula TlX_3(chelate)DMF. It is established that the DMF is co-ordinated to the thallium by infra-red evidence. More over the position of the Tl-X stretching bands for DMF complexes have moved to lower frequencies than for the TlX_3(chelate). The new dimethyl formamide complexes were also shown to be non-electrolytes in acetonitrile and dimethylformamide, and so the dimethyl formamide ligand is presumably still co-ordinated on the complex. It can be seen that the TlX_3(chelate)DMF complexes could easily have been formed from the TlX_3(chelate) complexes by rupture of one of the Tl-X bridged bonds followed by co-ordination of a DMF molecule. Let us consider the possible isomer of TlX_3(chelate)DMF which can be formed assuming first two dimeric structures 3.6a and 3.6b and then the polymeric one 3.6c. Since it was possible to obtain only one isomer of the DMF complex, structure 3.6d and 3.6e can be ruled out because on co-ordination of DMF, the bridged Tl-X band will break up giving two complexes. For the structure 3.6d and 3.6e the expected isomer would be one trans. and another cis-isomer and So the spectra of the above complexes would be made more complex than is observed. So the structures 3.6d and 3.6e are unlikely on the basis of chemical reasoning. This left three possible structures.

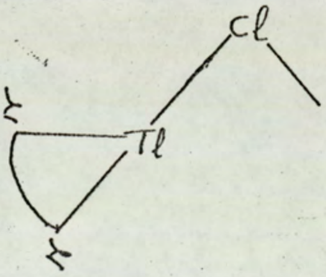
In table 3 the possible isomers of the DMF complexes are described.

TABLE 3

Structures in the figure	Centre of symmetry	Type of bridge[+] bond	Isomers on reaction with DMF cis or trans*
3.6a	yes	2	both cis & both trans*
3.6b	yes	1	both trans
3.6c	no	1	both cis
3.6d	no	2	cis and trans[±]
3.6e	no	2	cis and trans[±]



trans to Cl

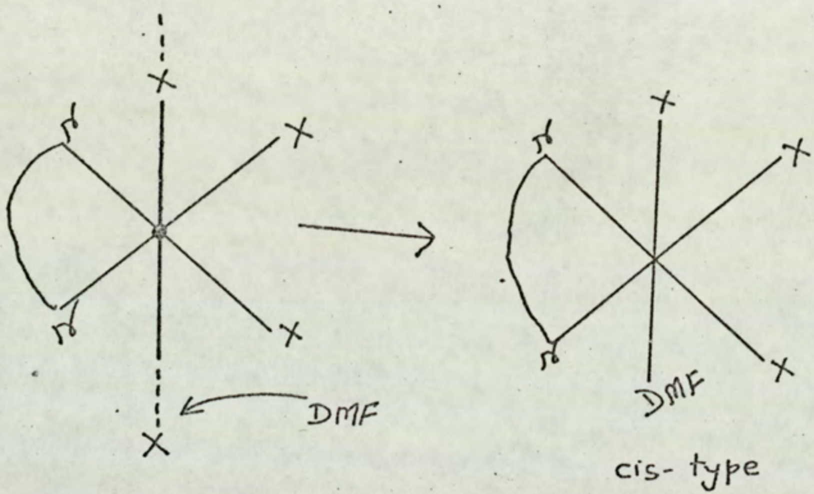


trans to N

* Either bonds with Cl(Br) trans to Cl or bonds with Cl(Br) trans to N will break, not both.

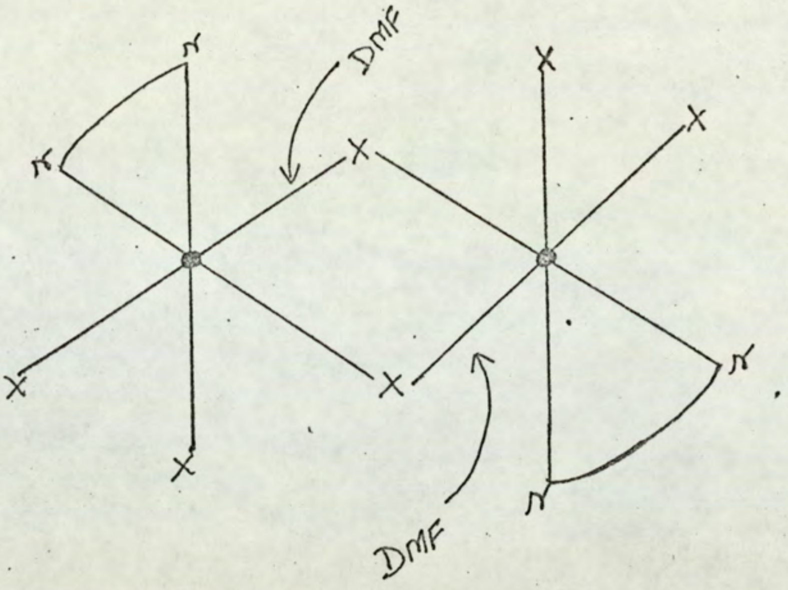
[±] Equal possibilities that reaction with DMF will lead to cis or trans.

So from the table 3 it can be seen that structures 3.6d and 3.6e can be ruled out. Also for the $TlCl_3$(tripyam)DMF it has been suggested that the complex has a cis-type structure, and also the $TlCl_3$(tripyam) has in fact cis-type structure with the C_{3v} symmetry. So the structure 3.6b can be ruled out as it gave both the trans isomer. This left only two possibilities for the structure of the TlX_3(chelate). Also earlier it has been ruled out the first two structures with the centre of symmetry. The structure 3.6a in fact gives two cis isomers on the formation of DMF complex but as it has a centre of symmetry it can be ruled out upon the spectroscopic evidence. So the author favoured the structure 3.6c and explained the formation of the DMF complex formation as follows



The polymeric bridge breakdown and the TlX_3(chelate)DMF formed as a cis-monomer.

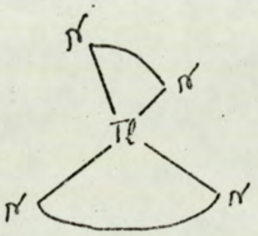
More recently Baxter and Gafner[42] reported the crystal structure of $TlCl_3$(Phen) complexes. More surprisingly they found that the above complex has a centrosymmetric dimeric structure. They reported that the thallium was six co-ordinated and the dimer was joined by the double chlorine bridges which consists of one short Tl-Cl bond and one long bond. The length of the later bond would seem to indicate that the pair forms a weak dimer. The complex molecule has a distorted octohectral structure. The dimer has a centre of symmetry and they represent the dimer as follows



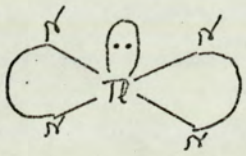
Also they described the reaction of dimethyl formamide which gave two units with co-ordinated DMF. This is exactly what the author argued about the structure of TlX_3(chelate) where the structure 3.6a gave two cis-isomer, but because of the co-incidences of the infra-red and Raman bands the structure 3.6a was eliminated, and the structure 3.6c, the polymeric structure was suggested. This problem raises caution about the wide use of vibrational spectroscopy. The author feels that for the heavy metal like thallium, some time the fundamental modes are so near that it could not be separable and so wrong conclusions could be made. Here the chemical approach leads to a correct structure, but the help of the vibrational spectroscopy only leads to the wrong conclusion.

Thallium (I) complexes with nitrogen donor ligands

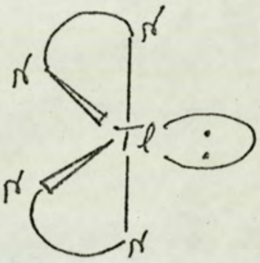
The thallium (I) complexes with 2,2'-bipyridyl and 1,10-phenanthroline were prepared. As described in the introduction, Kul'ba[22] suggested that the $Tl(bipy)_2ClO_4$, $Tl(phen)_2ClO_4$ and $Tl(phen)_2NO_3$ were 1:1 eletrolyte in solution. So the $[Tl(bipy)_2]^+$ and $[Tl(phen)_2]^+$ units may exist in all three complexes. The n.m.r. spectra of the $Tl(phen)_2ClO_4$ and $Tl(phen)_2NO_3$ in dimethyl sulphoxide (DMSO) show that the coupling constants for the proton on the ligands of the complexes and those for the protons of the free phenanthroline ligand were identical, but the chemical shifts were different[40]. This observation indicated that the phenanthroline was still co-ordinated to the thallium in dimethyl sulphoxide solution. The spectra also showed that each half of the penanthroline ligands were magnetically and chemically equivalent. Now considering the possible structure for the $[Tl(phen)_2]^+$ as shown in the introduction,



1.5a



1.5b



1.5c

in the tetrahedral (1.5a) and the squarepyramidal (1.5b) structures, the two halves of the phenanthroline ligands are magnetically equivalent, while in 5 - co-ordinated structure 1.5c the phenanthroline ligands are magnetically non-equivalent. Although the two halves of the phenanthroline ligand are magnetically non-equivalent in structure 1.5c, it is not possible to rule out the above structure. If some form of pseudo rotation occured then the ligands would still appear to be equivalent on the n.m.r. time scale. Pseudo rotation is the phenomenon which occurs when the phenanthroline ligands are "flipping" at such a rate that the spectrum is a time average of the two conformation and the ligands appear equivalent. However this has not been previously observed for a bulky phenanthroline systems and it seems unlikely that the rate of flipping here could be great enough to produce the effect. So the five co-ordinate structure 1.5c can be eliminated by the n.m.r. measurement.

Also the 1.5b is unlikely on steric ground since with the exception of $[Pd(phen)_2]^+$, no trans-bis (1-10 phenanthroline) complexes have been characterised. Also the experiments were carried out to find out whether $Tl(bipy)_2ClO_4$ exhibited any low Lewis basicity. The reactions between $Tl(bipy)_2ClO_4$ and BF_3 (Borontrifluoride) and also with $SbCl_5$ (antimonypentachloride) afford no additive complex. One would expect to form a complex of the type $[Tl(bipy)_2 \cdot Y]ClO_4$ ($Y = BF_3$ or $SbCl_5$) if the lone pair of electrons are stereochemically active. The infra-red spectra and analytical data show that no complex formation has occured. This suggests that the $6s^2$ electrons do not exhibit Lewis basicity in the $[Tl(bipy)_2]^+$ ion and so no chemical reaction takes place. It is known that the hexafluorotellurate (IV) is not significantly distorted[42a], indicates that it may be dangerous to assume that the electron pairs need always be stereochemically active. This observation suggests that the squarepyramid type 1.5b structure is unlikely.

These results favour structure 1.5a, where two halves of the phenanthroline ligands are equivalent and there is no stereochemical role for the $6S^2$ electrons. However there is the possibility that in dimethyl sulphoxide solution, thephenanthroline ligands are no longer co-ordinated. The results obtained for the $[Tl(phen)_2]^+$ ion in dimethyl sulphoxide show that the chemical shifts of the phenanthroline ligands were different from those reported for free phenanthroline in dimethyl sulphoxide solution suggesting that the ligands are still co-ordinated to thallium. So from the available chemical and spectroscopic results the tetrahedral structure for $[Tl(phen)_2]^+$ and $[Tl(bipy)_2]^+$ is more likely.

One recent paper[42b] reported the far infra-red spectra of $[Tl(phen)_2]Z$

(Z = NO_3^-, ClO_4^-) to 200cm^{-1} and made an assignment of thallium-nitrogen stretching ν(Tl-N) frequency close to 250cm^{-1}. The author obtained the spectra of the above complexes and found the spectra to be very simple to 80cm^{-1}. The most probable assignment for ν(Tl-N) suggested around 120cm^{-1} (table-1). Also the spectra of $[Tl(bipy)_2]ClO_4$ was found less satisfactory but here to the assignment of ν(Tl-N) suggested very close to 125cm^{-1}. The simplicity of the infra-red spectra of the above complexes appears to supplement the conclusion that the stereochemical environment of thallium (I) in these complexes is not very much distorted.

D. THALLIUM (I) COMPLEXES WITH SULPHUR DONOR LIGANDS

The complexes of thallium (I) with thiourea and substituted thiourea were prepared. The srystal structure of the thiorea complexes with thallium (I) salts was reported[32] (fig1-4). The infra-red and Raman spectra were obtained for the above complexes (table 2a). The quality of the spectra is not good but it was possible to assign thallium-sulphur ν(Tl-S) stretching frequency.

The vibrational spectroscopic data was not reported for thallium (I) thiourea complexes or other complexes with sulphur donor ligands, so the assignment of ν(Tl-S) produced some difficulty. On the other hand the infra-red spectra of $Pb(TU)_4Cl_2$ was reported. Adams and Cornell[42c] reported the ν(Pb-S) stretching frequency around 165-171cm^{-1} for $Pb(TU)_4Cl_2$ Thallium has a similar mass to lead and chlorine has a similar mass to sulphur so the ν(Tl-S) should occur in a similar region. But here the thallium is in oxidation state +1 and the crystal structure of thallium(I) thiourea suggests that the thallium is 8-co-ordinated, and the Tl-S bond length is 3.43A^{o}, the sulphur is acting as a bridging group. So considering the above factors, the ν(Tl-S) stretching frequency would appear in a lower region than expected.

Also the crystal structure shows the long Tl-S bond length, becuase of the ionic dipole the lattice vibration also might occur in this region, and so it would be dangerous to assign ν(Tl-S). But attempt was made to assign to ν(Tl-S) as indicated in the table 2a. The other strong band around 32ocm^{-1} in the case of hexahydropyrimidine 2-thione ligand is a ligand band, and it also appeared in the free ligand. No other bands were assigned.

From the simple spectra of the above complexes it is suggested that all the complexes have similar structure. The introduction of cyclic thiourea ligands does not appear to change the structure considerably but this can only be confirmed by detailed X-ray crystal structure.

SPECTROSCOPY AND CHEMISTRY OF ORGANOTELLURIUM COMPOUNDS

CHAPTER 4

INTRODUCTION

Tellurium belongs to group 6b i.e. the oxygen group. The atoms of these elements have six electrons in the ns and np orbitals of the valency shell . With electronic structures approaching the configurations of the next inert gas atoms, the elements show purely non-metallic chemistry except for polonium and to a very slight extent tellurium. All the elements in this group give rise to simple anions S^{2-}, Se^{2-} and Te^{2-} which form salts with cations of the alkali metals or alkaline earth metals. All the elements combined with metals less electropositive than the alkaline earth metals to form crystalline compounds with giant molecular structures. The sulphides in general have less simple structures than the oxides, and the selenides and tellurides are more like alloys than are oxides or sulphides.

Tellurium exists in two forms, one crystalline and the other amorphous. The crystalline form is metallic, has a bright luster like antimony, but it is brittle and easily powdered. The electronic configuration of the valency shell of the tellurium atom in the ground state is

5s	5p	5p	5p	5d	5d	5d	5d	5d
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$					

The 5s electron pair is inert in $[TeCl_6]^{2-}$

Tellurium forms many compounds of the general formula TeX_4. These compounds may be telluronium compounds $[TeX_3]^+X^-$ or they may contain a tellurium atom in the trigonal bipyramidal valence state with one hybrid orbital occupied by a lone pair of electrons.

Tellurium forms many compounds with halogens in the oxidation state 2+. 4+ and 6+. But of the halogens only fluorine forms stable compounds with the element in its sexivalent state. The sexifluoride is most volatile of these halides since in this, the central tellurium atom is very effectively screened by the fluorine. The TeF_6 forms additive compounds with alkali halides and also with silver and barium halides. Glifford and Morris[43] suggested that the $AgTeF_7$ and $BaTeF_8$ might have a co-ordination number seven, thus they described the compound $BaTeF_8$ as $[BaF]^+[TeF_7]^-$.

Tellurium forms dihalides with chlorine and bromine. The structure of these halides is uncertain, but it is probable that the tellurium atom is in the tetrahedral valence state, two of the hybrid orbitals being occupied by the lone pairs of electrons. They form complexes with thiourea (TU) and substituted thiourea with the formulae $Te(TU)_2X_2$ and $Te(Tu)_4X_2$ [44]. The characteristic stereochemistry for Te^{2+} is square planar but for $Te(Me_4Tu)_2Cl_2$ (Me_4Tu = tetramethyl thiourea), there appears to be only three normal bonds, the fourth (to the chlorine of an adjacent molecule) being very long so that the complex is virtually three co-ordinate.

The most stable of all the halogen derivatives are the Te(IV) halides. Tellurium forms a number of compounds of the type TeX_4. There are the four tellurium tetrahalides, and representative at least of the derivatives $RTeX_3$, R_2TeX_2 and R_3TeX (R = alkyl, or aryl groups). The structure of the tetrahalides of the tellurium has been the subject of considerable controversy. If the lone pair of the central tellurium atom of such a tetrahalide molecule is stereochemically active, valency theory[45] predicts a trigonal bipyramidal arrangements of the bonding pairs and lone pair, with the lone pair at one of the equatorial positions. This results in a molecule of C_{2v} symmetry, with two pairs of equivalent axial and equatorial halogen atoms.

Tellurium tetrahalide is sufficiently stable to exist in the vapour state. Stevenson and Schomaker[46] made electron diffraction investigations and suggested that in the vapour phase the $TeCl_4$ has a trigonal bipyramidal structure with the lone pair located at one of the equatorial position. The structure of the compound in the vapour state does not allow one to predict the solid state geometry, e.g. compounds which are unimolecular in the gaseous state can rearrange into ion aggregates upon condensation as solids, and one must rely on physical investigation of the solid state for evidence of its structure. The Raman spectra of the solid $TeCl_4$ and molten $TeCl_4$ suggested an ionic structure $TeCl_3^+$ Cl^- in which the cation has pyramidal (C_{3v}) symmetry[47]. Also the structures in solid state and in molten state were identical. Adams and Lock[48] measured the infra-red and Raman spectra of solid and its benzene solution and they agreed that in the solid state the spectra were consistent with the ionic formulation, but in benzene solution the infra-red spectrum supported the monomeric trigonal bipyramidal structure. Also the observation that molten tellurium tetrachloride conducts electricity[49] has also been considered in support of an ionic structure.

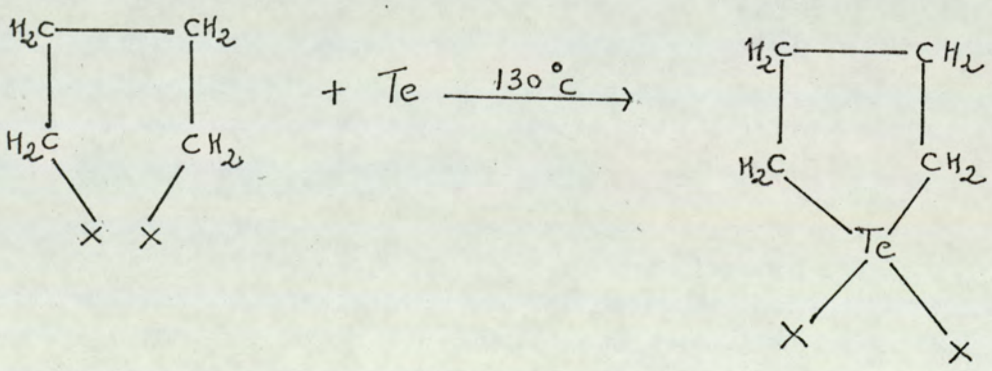
On the other hand the observation of six ^{35}Cl nuclear quadrupole resonances in two groups of three frequencies for $TeCl_4$ was thought to indicate the presence of trigonal bipyramidal molecule[50]. Hayward and

Hendra[51] measured the infra-red and Raman spectra of $TeCl_4$ and $TeBr_4$ and suggested that both the compounds have similar structures. Also they suggested that the TeX_4 (X = Cl or Br) might have a slightly distorted trigonal bipyramidal structure. The infra-red and Raman spectra of solid $TeCl_4$ ruled out the presence of monomeric $TeCl_4$ of C_{2v} symmetry[55]. Also Beattie[52] reported that molten $TeCl_4$ has the conductivity of a salt, the most obvious explanation of the physical properties was in terms of ionisation to species such as $TeCl_3^+Cl^-$ or $TeCl_3^+$ $TeCl_5^-$. Since the solid is colourless and did not show evidence for $TeCl_5^-$ in the infra-red spectrum, they agreed with an ionic formulation $TeCl_3^+Cl^-$. Greenwood and his co-workers[53] also agreed with the ionic formulation according to the infra-red spectra, but later[54] more detailed molecular weight measurement in benzene and toluene suggested that $TeCl_4$ behaved as a trimer in a less than 0.3% solution but on increasing the concentration above 2%, it shows a molecular weight very near to a tetramer. The infra-red spectra in benzene ruled out the C_{2v} structure but they suggested that the spectra should be interpreted in terms of an associated bridged species. So with the molecular weight data Greenwood suggested that the $TeCl_4$ has a bridged polymeric structure with $TeCl_3{}^+ Cl^-$ as one of the species.

More recently crystal structure of tellurium tetrachloride by complete X-ray analysis was reported by Buss and Krebs[56]. According to them the solid consists of isolated Te_4Cl_{16} units with a cubane like structure. The co-ordination of Te atom was made up to an octahedron by three much more remote bridging Cl atoms and three terminal Cl atoms forming the base.

Compounds in which there is a chemical bond between carbon and selenium and tellurium, range from the simple carbon selenides such as CSe_2 and CSSe and the telluride CSTe, to molecules such as selenanthrene, telluranthrene and even more complex species. The thermal stabilities of the organo compounds of the oxygen group elements decreases with increasing atomic number and their stability to oxidation increases so much so that the alkyl tellurides react quite readily with oxygen at room temperature.

Although tellurium tetrachloride is widely used for syntheses leading directly to organotellurium compounds, tellurium powder itself is also a useful starting material. So dialkyl tellurium diiodide was synthesised by reacting tellurium powder and alkyliodide[57]. But sulphur or selenium did not behave in the same manner[58]. Methyl iodide reacts with tellurium powder in sealed tubes to produce Me_2TeI_2. Cohen and his co-workers[59] obtained bis(perfluorophenyl)telluride from tellurium and iodopentafluorobenzene. Heterocyclic compounds were obtained by the reaction of amorphous tellurium dissolved in tetramethylenediiodide at 130°C with a quantitative production of tetracyclopentane 1-1-diiodide[60].



The reaction was also found favourable for dibromide and dichloride. So tetramethylenedibromide and pentamethylene chloride gave cyclic dihalides[61] The reactivity of dihalides decreased with decreasing atomic mass.

When sodium telluride was used in place of tellurium better results were obtained for these cyclic compounds. When tetraphenyl tin and tellurium powder was heated at 310°C a mixture of diphenyltelluride tin metal and telluranthrene was obtained[62]. Also when hexachlorobutadiene was heated with tellurium powder, tetrachloro tellurophene was obtained in a good yield[63].

Tellurium also reacts readily with Grignard reagents and organoalkali compounds. Thus tellurium reacted with phenyl magnesium bromide to give diphenyl telluride and hydrogen telluride[64]. Giua and Cherchi[64] suggested that the mechanism of the above reaction as:

$$C_6H_5MgBr + Te \longrightarrow C_6H_5TeMgBr$$

$$2C_6H_5TeMgBr \longrightarrow (C_6H_5)_2Te + (BrMg)_2Te$$

$$(BrMg)_2Te + HCl \longrightarrow H_2Te + 2MgBrCl$$

In fact they reported the formation of H_2Te during the experiment.

Petragnani and De. Moura Campos[65] proposed the fllowing mechanism for the reaction.

$$2C_6H_5MgBr + Te \longrightarrow C_6H_5TeMgBr$$

$$2C_6H_5TeMgBr + Te \longrightarrow C_6H_5Te . TeC_6H_5 + Te(MgBr)_2$$

$$C_6H_5\text{-}Te\text{-}Te\text{-}C_6H_5 + C_6H_5MgBr \longrightarrow C_6H_5TeC_6H_5 + C_6H_5TeMgBr$$

The reason for this mechanism was explained and they reported the formation of mixed diphenyltelluride and diphenylditelluride. But on the other hand the formation of $C_6H_5TeMgbr$ was doubtful as the reaction mixture did not react with ethyl iodide to form phenyl ethyl telluride. Bowden and Braude[66] reported the preparation of the above compound using $C_6H_5TeMgBr$. Waters[67] suggested the free radical mechanism of diphenyl telluride during the reaction of diazonium salt with tellurium. So Petragnani[65] suggested the similar free radical mechanism for the Grignard reagent and tellurium

$$\begin{array}{lcl}
2C_6H_5MgBr & \longrightarrow & 2C_6H_5^{\bullet} + BrMg^{\bullet} \\
2C_6H_5^{\bullet} + 2Te & \longrightarrow & 2C_6H_5Te^{\bullet} \\
2C_6H_5Te^{\bullet} & \longrightarrow & C_6H_5TeTeC_6H_5 \\
2BrMg + Te & \longrightarrow & Te(MgBr)_2 \\
\hline
\multicolumn{3}{l}{2C_6H_5MgBr + 3Te \longrightarrow C_6H_5Te\ Te\ C_6H_5 + Te(MgBr)_2}
\end{array}$$

followed by

$$\begin{array}{l}
C_6H_5Te\ Te\ C_6H_5 \longrightarrow 2C_6H_5Te^{\bullet} \\
2C_6H_5Te^{\bullet} + 2C_6H_5MgBr \rightarrow 2C_6H_5\text{-}Te\text{-}C_6H_5 + 2MgBr \\
2BrMg^{\bullet} + Te \longrightarrow Te(MgBr)_2 \\
\hline
C_6H_5\text{-}Te\text{-}Te\text{-}C_6H_5 + 2C_6H_5MgBr + Te \longrightarrow 2C_6H_5\text{-}Te\text{-}C_6H_5 + Te(MgBr)_2
\end{array}$$

The existance of $Te(MgBr)_2$ in the reaction mixture was suggested by the formation of tellurium with water

$$\begin{array}{lcl}
Te(MgBr)_2 + H_2O & \longrightarrow & H_2Te + 2MgBr(OH) \\
H_2Te + \tfrac{1}{2}O_2 & \longrightarrow & H_2O + Te
\end{array}$$

The reaction between amorohpus tellurim and phenyl lithium was also described[65]. In absolute ether tellurium reacts with phenyl lithium to form Te, Ph_2TeCl_2 and $PhTeCl_3$. Also the reaction between tellurium and diorgano mercury compound is known[68,69,70]. Dibenzotelluride was prepared in a good yield using tellurium powder and biphenylenemercury[71]. Using diorganomercury compounds and tellurium, Ph_2Te[68], (o.Tolyl)$_2$Te[72,73] (p.tolyl)$_2$Te[72,73], (pentafluorophenyl)$_2$Te[59] were obtained in a good yield. Reaction of elemental tellurium with diagonium salts has been reported to prepare diaryl tellurium dihalide and diaryl telluride[67,74]. Taniyama[74] thus prepared about fifteen diaryl tellurium dihalides.

Diphenyliodonium chloride when reacted with sodium carbonate, tellurium powder and ether, then shaken with aqueous solution of thioglycolic acid at room temperature, produced diphenyl telluride in a good yield[76]. The same result was obtained when the reaction mixture was shaken with aqueous H_2S[76]. If the reaction product was treated with bromine diphenyl tellurium dibromide was obtained. When p.tolyliodonium chloride was reacted with tellurium and then brominated bis(p.tolyl)tellurium dibromide was obtained. Fusion of tellurium and diphenyliodonium chloride gave diphenyl tellurium dichloride.

Tellurium tetrachloride is the best starting material for the preparation of organotellurium compounds. 1, 3-diketones react with tellurium tetrachloride to form cyclic and linear condensation products. Tellurium tetrachloride also forms condensation products with p.methoxyphenyl and p.ethoxyphenyl groups. Morgan and Kellet[77] reported the preparation of p.methoxyphenyl tellurium trichloride, bis(p.methoxyphenyl)tellurium dichloride, bis(p.methoxyphenyl)ditelluride, and bis(p.methoxyphenyl) telluride. Also Morgan and Drew[78] reported the preparation of p.ethoxyphenyl tellurium trichlordie, bis(p.ethoxyphenyl)ditelluride, bis(p.ethoxyphenyl)tellurium dichloride and bis(p.ethoxyphenyl)telluride.

The interaction of tellurium tetrachloride with a grignard reagents yield bis(organo)tellurium dihalides, bis(organo) tellurides and tris (organo) tellurium halides. The mechanism of this reaction is unknown but Lederer[79] has postulated that the tellurium tetrachloride is first reduced by the Grignard reagent, then it reacts with further Grignard reagent to produce the above compounds.

$$TeCl_4 + RMgBr \longrightarrow Te + 4MgClBr + 2R_2$$

Lederer described the formation of R_2Te in the following way. First tellurium tetrachloride reacts with the Grignard reagent to form R_3TeCl or R_3TeBr, which on further reaction with Grignard forms R_2Te.

$$TeCl_4 + 3MgBr \longrightarrow \begin{matrix} R_3TeCl \\ \text{or} \\ R_3TeBr \end{matrix} + 3MgClBr$$

$$R_3TeX + RMgBr \longrightarrow R_2Te + R_2 + MgBrX$$

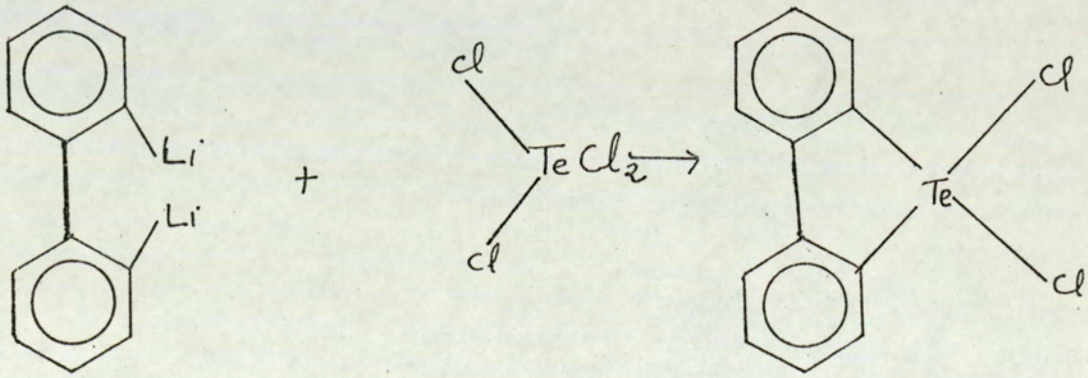
$$(\text{where } X = Cl \text{ or } Br)$$

$$TeCl_4 + 4RMgBr \longrightarrow R_2Te + R_2 + 4MgBrCl$$

In fact Lederer obtained the R_3TeX type compounds (where R = phenyl, o - tolyl and X = iodine) when the reaction product was treated with KI. Later Rheinboldt and Petragnani[80] prepared R_2Te using tellurium tetra chloride and RMgX (R = phenyl) in the ratio of 1:5 after refluxing the reaction mixture, and believed that no side reaction took place. During this reaction tellurium was formed which reacted with the grignard reagent. Rheinboldt and Petragnani observed that when a reaction mixture of5:1 Grignard reagent to tellurium tetra chlordie was not refluxed, but kept cold and then hydrolysed, triorganotellurium halides were formed. Tellurium tatra bromide and tetra iodide gave much higher yields (90.8% and 96% respectively compared to 88% in the case of tellurium tetra chloride) of R_2TeCl_2 (after reaction with SO_2Cl_2).

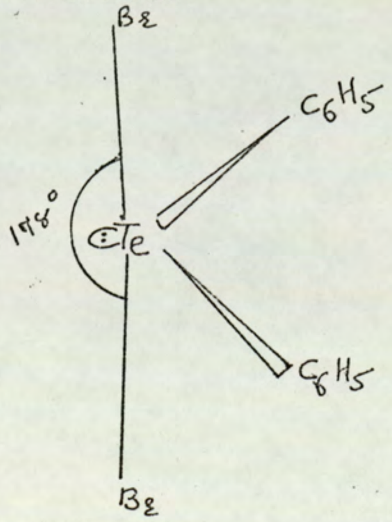
Tellurium tetrachloride reacts with an organomercuric chloride. The following compounds $C_6H_5TeCl_3$ [81], $CH_3C_6H_4TeCl_3$ [81], 2- $C_{10}H_7TeCl_3$ [82] etc. were prepared by using organomercuric compounds. Organolithium and organozinc compounds are also reactive in the presence of tellurium tetrachloride to give the corresponding organotellurium compounds. Tetraphenyl tellurium was obtained by the reaction between tellurium tetrachloride and lithium bromide free phenyl lithium solution in ether[83]. Also when perfluorophenyl lithium was allowed to react with tellurium tetrachloride about 30% of bis(pentafluorophenyl)tellurium (II) was obtained[59]. The preparation of tetrabutyl and tetramethyl tellurium was also reported[84].

Tellurium tetrachloride is used to obtain the heterocyclic compounds containing tellurium atom . When 2,2' dilithiodiphenyl reacted with tellurium tetrachloride bis(phenylene)-tellurium dichloride was obtained as a yellow crystalline product.



Tetraphenyl tellurophene was also obtained by the reaction of tellurium tetrachloride and 1,2 dilithiotetraphenyl butadiene[86]. Mack[87] reported the preparation of tellurophene by the reaction of diacetylene with sodium telluride.

Structural investigations of the organotellurium compounds are limited. Only a few compounds have been studied by either spectroscopy or by X-ray analysis. Infra-red and Raman spectra of dimethyl tellurium dihalides have been reported[88,89], and the assignemtns of tellurium methyl group, and tellurium halogen stretching vibrations were made according to its trigonal bipyramidal structure[90]. The dimethyl tellurium dihalides have a slightly distorted ψ- trigonal bipyramidal type structure with one equatorial position occupied by one lone pair of electron. The crystal structure of diphenyl tellurium dibromide was discussed by Christofferson and McCullough[91]. The structure of the above compound was also slightly distorted ψ-trigonal bipyramidal type with possibly a C_{2v} symmetry. The two axial postions were occupied by the halogen and the equatorial position occupied by two phenyl groups and one lone pair of electrons.

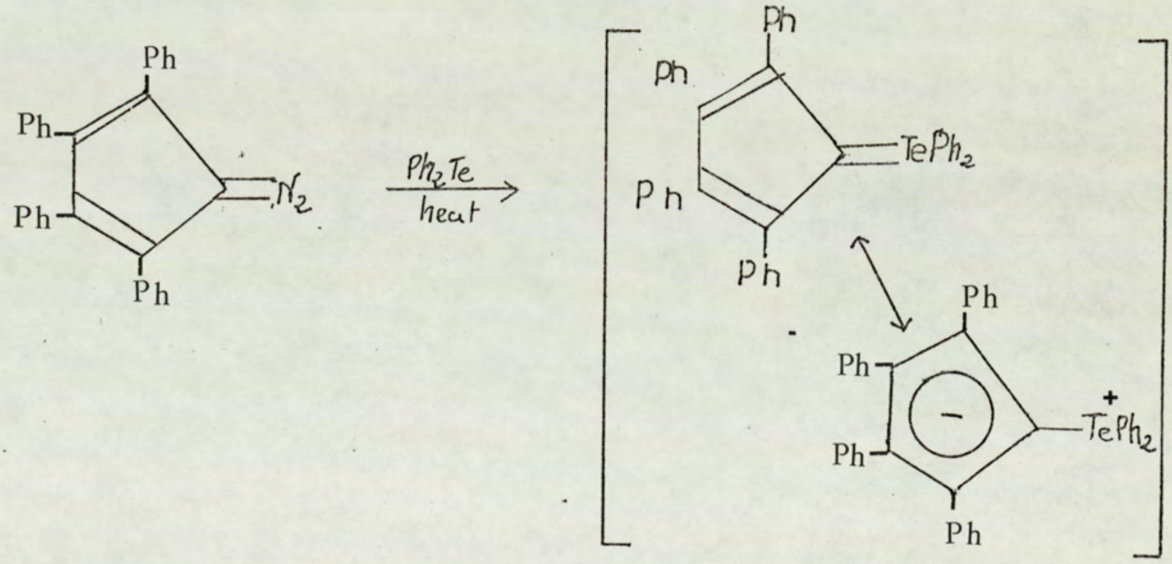


Also the crystal structure of di(p.tolyl)telluride was reported by

Blackmore and Abrahams[92]. The structure was shown to be V-shpaed with C_{2v} symmetry.

The infra-red spectra of the arylorgano tellurium compounds were reported. Fritz and Keller[93] studied series of organo tellurium compounds including diaryl tellurium dihalides down to 250cm^{-1}. The assignment of the tellurium phenyl stretching vibration was made between 455 to 487cm^{-1} No further details of the infra-red spectra have been described.

Although sulphonium[94] and selenonium[95] ylides have been prepared no tellurium ylides were known until recently when Freeman and Lloyd[96] reported the preparation of the first telluronium ylides. They reacted diazotetraphenylcyclopentadiene with diphenyl telluride in the presence of an appropriate carbene acceptor:



During the present work diaryl tellurium dihalides were prepared, and detailed infra-red, Raman and n.m.r. measurements were made. Attempts were also made to prepare new telluronium ylides.

CHAPTER 5

EXPERIMENTAL

Preparation of organo-tellurium compounds.

Preparation of diphenyl telluride and its halogen derivatives,

Diphenyl telluride can be prepared by many methods. But the process described by Rheinboldt and Petragnani[80] produces high percentage yields. When a Grignard reagent was treated with a suspension of tellurium tetrachloride, (about 88%) diphenyl tellurium dichloride (after reaction of the crude telluride with sulphuryl chloride) was formed. However, during the hydrolysis they found the formation of free tellurium.

When tellurium tetrachloride solution was added to the ice cold Grignard reagent, then refluxed and finally hydrolysed, no tellurium formation was observed. So with the slight alteration diphenyl telluride was prepared as follows.

The Grignard reagent was prepared by placing magnesium metal (6.1gms) in a three necked round bottomed flask equiped with a condenser and a dropping funnel. The metal was covered with sodium dried ether and from the dropping funnel bromobenzene (39.3gm) in dry ether (60ml) was added drop by drop. After addition of all the bromobenzene solution, the Grignard reagent was refluxed for 30 minutes. The reaction mixture was then cooled and dry ether (100ml) and dry benzene (200ml) was added. The flask was kept in an ice bath and the contents were mechanically stirred. The temperature of the mixture was kept below $0^{o}C$ all the time. A solution of tellurium tetrachloride (13.5gm) in benzene (300ml) was placed in the dropping funnel. To the ice cold stirred Grignard reaction mixture, the tellurium tetrachloride solution was added very slowly so that no free tellurium was formed in the reaction mixture. In one hour the tellurium tetrachloride was added to the Grignard reagent. The colour of the reaction mixture changed from green to light yellow after all the tellurium tetrachlorde has been added. The stirring was maintained for another 30 minutes at room temperature and then the mixture was refluxed for two hours.

After two hours the reaction mixture was cooled and hydrolysed with ice cold saturated ammonium chloride solution (300ml). The mixture was stirred for 10 minutes and then filtered. The filtrate was collected and the organic layer was separated and washed three times with distilled water (200ml), and dried over anhydrous magnesium sulphate in a flask. The dried yellow solution was then taken into a flask and all the organic solvents were distilled off in a rotatory vacuum evaporator. The residue, a dark yellow orange coloured liquid, was collected. - yield of the crude product was 18.5gms. The product contains some biproduct such as diphenyl To obtain the pure diphenyl telluride the crude product was first brominated and then the diphenyl tellurium dibromide was reduced by sodium sulphide as follows.

The crude product was dissolved in carbon tetrachloride (100ml) and bromine solution in carbon tetrachloride was added dropwise with constant stirring until all telluride was oxidized. The yellow solid was collected and washed with carbon tetrachloride and then with ether and dried in air - yield 20.4gms. The diphenyl tellurium dibromide was recrystallized from benzene which gave bright yellow crystals M.P.201°C (lit. M.P. 198 - 200°C) - yield 17.6gm.

Found : C, 32.3; H, 2.3, calculated for $C_{12}H_{10}Br_2Te$, C, 32.6; H, 2.7%,

Reduction of diphenyl tellurium dibromide to diphenyl telluride.

The crystalline diphenyl tellurium dibromide (15gms) was taken into a flask, and hydrated sodium sulphide (40gms) was added to it and the mixture was heated at 80 - 90°C in a water bath for 45 minutes. The telluride was formed as a dark yellow liquid. The mixture was cooled and the sodium sulphide solution was removed. The diphenyl telluride was dissolved in ether (200ml) and the ethereal solution was washed four times with distilled water to remove any trace of sodium sulphide. The yellow solution was dried over $MgSO_4$ in a flask. The dried ethereal solution was taken into a flask and all the solvent was removed by rotatory vacuum evaporator. The light yellow liquid left behind was collected - yield 8.5gms.

Preparation of diphenyl tellurium dichloride - Pure diphenyl telluride (3.5gm) was dissolved in carbon tetrachloride (25ml) and excess of sulphuryl chloride (SO_2Cl_2) in carbon tetrachloride (10ml) was added with constant stirring. A white crystalline product was formed which was filtered, washed with a little carbon tetrachloride and dried in a desiccator. - yield 4.1gms The diphenyl tellurium dichloride was recrystallized from benzene which gave bright white crystals. M.P. 160°C (lit. M.P. 158-161°C).

Found : C, 40.1; H, 3.2; calculated for $C_{12}H_{10}Cl_2Te$ C, 40.9; H,2.8%.

Preparation of diphenyl tellurium diiodide - Pure diphenyl telluride (3.5 gms) was dissolved in carbon tetrachloride (25ml) and to this solution iodine (4gms in 150ml carbon tetrachloride) was added until the precipitation was completed. The brown solid settled down and the clear solution became yellow. The solid was filtered, washed with carbon tetrachloride and dried - yield 6.1 gms. The diphenyl tellurium diiodide was recrystallized from hot carbon tetrachloride. On cooling the solution slowly red brown crystals were formed. m.p. 235°C (lit.[80] m.p.234-236°C)

Found: C,27.1; H,1.9; calculated for $C_{12}H_{10}I_2Te$, C,26.9; H,1.9%

Preparation of di(o.tolyl)telluride and its halogen derivatives - Two different procedures are known for the preparation of di(o.tolyl)telluride Lederer[97] prepared di(o.tolyl)telluride from the Grignard reagent reacted with tellurium dibromide. Taniyama[74] prepared di(o.tolyl)tellurium dichloride from the tellurium and a diazonium salt, but the later procedure did not give a higher yield, so Lederer's process was used to prepare the telluride with slight alteration. The Grignard reagent was prepared from o.bromotoluene (43gms) and the reaction mixture was refluxed for three hours. The same procedure was followed as the preparation of diphenyl telluride. But when the final reaction mixture was hydrolized with saturated ammonium chloride solution a small amount of free tellurium was formed. The crude di(o.tolyl) telluride (20.5gms) was dissolved in carbon tetrachloride (150ml) and bromine solution in carbon tetrachloride (40ml) was added dropwise with constant stirring until all the telluride was brominated. Some solvent was removed by a slow evaporation and then left for crystallization. After some time yellow crystals were formed, which were then filtered, washed with a little carbon tetrachloride and dried in the air. - yield 22gms. The di(o.tolyl)tellurium dibromide was recrystallized from hot carbon tetrachloride m.p. 182°C (lit[98] m.p. 182°C)
Found : C, 34.5; H,3.0, calculated for $C_{14}H_{14}Br_2Te$, C, 35.8; H,3.0.

Reduction of di(o.tolyl)tellurium dibromide to di(o.tolyl)telluride - The same procedure was followed as described for the reduction of diphenyl tellurium dibromide to diphenyl telluride (p. 77). The di(o-tolyl) tellurium dibromide (15gms) was reduced by sodium sulphide. The pure telluride was extracted as a light yellow solid - yield 10.6 gms, M.P. 36^{o}C (lit[97] M.P. 37-38^{o}C)

Preparation of di(o.tolyl)tellurium dichloride - The di(o.tolyl) telluride (3gms) was dissolved in carbon tetrachloride (20ml) and oxidized by sulphuryl chloride. The white crystalline product was collected and recrystallized from benzene - yield 4.0gms M.P. 183^{o}C (lit.[97] M.P. 184-185^{o}C) Found : C, 43.9; H, 3.7; calculated for $C_{14}H_{14}Cl_2Te$, C, 44.1; H, 3.7%.

Preparation of di(o-tolyl)tellurium diiodide - The di(o-tolyl)telluride (3gms) was dissolved in carbon tetrachloride (20ml) and a slight excess of iodine solution was added with constant stirring. A brown red solid was formed which then was filtered, washed with a little carbon tetrachloride and dried in the air. On recrystallization from hot carbon tetrachloride, dark brown-red crystals were obtained - yield 4.8gms. M.P. 175^{o}C (lit.[97] M.P. 176)

Found: C, 30.5; H, 2.5, calculated for $C_{14}H_{14}I_2Te$, C, 29.7; H, 2.5%.

Preparation of di(p.tolyl)telluride and its halogen derivatives[97] - The same procedure was followed as described for the preparation of di(o.tolyl) telluride. The Grignard reagent was prepared from 43gms of p.bromotoluene and the reaction mixture was refluxed for three hours. The crude di(p.tolyl) telluride was obtained as a light yellow solid - yield 23.5gms. This crude telluride was dissolved in carbon tetrachloride (150ml) and bromine (13 gms) solution was added with constant stirring. The yellow solid settle down at the bottom and the clear solution was removed carefully. The solid was washed with a little carbon tetrachloride and filtered, and dried in the air. The di(p.tolyl)-tellurium dibromide was recrystallized from benzene and light petroleum . . - yield 24gms. m.p. 197°C (lit m.p. 198 - 204°C) Found : C,35.6; H,3.0, calculated for $C_{14}H_{14}Br_2Te$, C,35.8; H, 3.0%.

Reduction of di(p.tolyl)tellurium dibromide to di(p.tolyl)telluride - The pure di(p.tolyl)tellurium dibromide (15gms) was reduced by sodium sulphide as described earlier. The crude product was extracted with benzene, and all the solvent was removed by vacuum rotatory evaporator. The telluride was recrystallized from methanol - yield 8.5gms. m.p. 64°C (lit[72] 63-64, Lederer reported m.p.69-70 but the author agrees with Zeise's[72] earlier determination).

Preparation of di(p.tolyl)tellurium dichloride - The di(p.tolyl)telluride (3gms) was dissolved in carbon tetrachloride (20ml) and oxidized by sulphuryl chloride. The white crystalline product was collected and recrystallized from benzene. - yield 3.8gms m.p. 160-162°C (lit[97] 164-164) Found : c,43.4; H,3.9, calculated for $C_{14}H_{14}Cl_2Te$, C,44.1; H,3.7%

Preparation of di(p.tolyl)tellurium diiodide - The di(p.tolyl)telluride (3gms) was dissolved in carbon tetrachloride (20ml) and excess of iodine solution in carbontetrachloride (20ml) was added until a brown solid was formed. The solid was filtered, collected and recrystallized from hot carbon tetrachloride m.p. 214° (lit[97] 218-219°C)
Found: C, 32.4; H, 2.7 calculated for $C_{14}H_{14}I_2Te$, C,29.81; H,2.5%.

Preparation of di(p.methoxyphenyl)tellurium dihalides and di(p-methoxyphenyl)telluride - Di(p.methoxyphenyl)tellurium dichloride was prepared from the reaction of anisole and tellurium tetrachloride following the

method of Morgan and Kellett[77]. Tellurium tetrachloride (15gms) and anisole (30gms) were heated for 24 hours at 150 - 180°C, the solution being afterwards allowed to solidify in a vacuum. The crystalline product was separated and recrystallized from benzene-Pet.ether as a colourless prisms. The yield of di(p.methoxyphenyl) tellurium dichloride was 12.5gms (about 95^{1}) m.p. 181°C (lit.m.p. 181-182)
Found : C,40.7; H, 3.5; calculated for $C_{14}H_{14}Cl_2O_2Te$; C, 40.7; H,3.4%

Reduction of di(p.methoxyphenyl)tellurium dichloride to di(p.methoxy - phenyl)telluride.

The method for the reduction of $(CH_3OC_6H_4)_2TeCl_2$ is tedious[78], hence the following new method was developed. The di(p.methoxyphenyl)tellurium dichloride (10gms) was dissolved in benzene (50ml) and a saturated solution of potassium metabisulphite (60ml) was added to it and the mixture was stirred for four hours at room temperature. The organic layer was separated and washed with distilled water. The benzene solution was collected and benzene was removed by slow evaporation. The crude telluride left behind a slight yellow solid which then recrystallized from aqueous alcohol - yield 6.5gms about 80% (lit[78] yield 37%) m.p. 54°C (lit[78] m.p. 53 - 54°)
Found : C, 47.4; H, 4.3 calculated for $C_{14}H_{14}O_2Te$; C, 47.9, H. 4.0%

Preparation of di(p.methoxyphenyl)tellurium dibromide - Di(p.methoxy phenyl)telluride (5gms) was dissolved in carbon tetrachloride (20ml) and bromine solution in carbon tetrachloride (10ml) was added with stirring. Di(p.methoxyphenyl)tellurium dibromide separated as light yellow crystals - yield 10gms. m.p. 190°C (lit m.p. 190°).

Found : C, 32.9; H, 2.8 calculated for $C_{14}H_{14}Br_2O_2Te$: C, 33.5; H,2.8%

Preparation of di(p.ethoxyphenyl)tellurium dihalides and di(p.ethoxyphenyl)telluride. - The di(p.ethoxyphenyl)tellurium dichloride was prepared following the method of Morgan & Drew[78]. Tellurium tetrachloride (22gms) was mixed with phenetole (95gms) and the mixture was refluxed for eight hours at 180 - 190°C on an oilbath. Hydrogen chloride was evolved and the addition of Pet.ether to the cold mixture caused the deposition of bis.p.phenetyltelluridichloride, which was purified by recrystallization from methanol. The dichloride formed colourless, glistening, prismatic needles. Yield 20gms. m.p.108° (lit.[78] m.p.108)
Found : C,42.6; H, 4.16, calculated for $C_{16}H_{18}Cl_2O_2Te$: C, 43.5, H,4.08%

Reduction of di(p.ethoxyphenyl)tellurium dichloride to di(p.ethoxyphenyl) telluride - The di(p.ethoxyphenyl)tellurium dichloride (15gms) was dissolved in benzene (80ml) and to this solution a saturated solution of potassium metabisulphite (60ml) was added and the mixture was stirred for six hours at room temperature. The organic layer was separated and washed three times with distilled water. The solvent was evaporated and the residue was crystallized from aqueous methanol. This new procedure of reduction afforded higher percentage yield than the described literature[78] procedure and also the time of the reduction was reduced to 25% The yield of di(p.ethoxyphenyl) telluride was 10.2gms (about 90%) m.p. 64°C (lit[78] m.p. 64°)
Found : C, 53.21; H, 4.96 calculated for $C_{16}H_{18}O_2Te$: C, 51.9; H, 4.87%

Preparation of di(p.ethoxyphenyl)tellurium dichloride - Di(p.ethoxyphenyl) telluride (4gms) was dissolved in carbon tetrachloride (30ml) and to this slight excess of bromine solution in carbon tetrachloride was added. The yellow solid was filtered, washed with cold carbon tetrachloride and dried.

The dibromide was recrystallized from hot carbon tetrachloride. Yield 5.2gms m.p. 127°C (lit[78]m.p. 127°C).

Found : C,35.94; H,3.59 calculated for $C_{16}H_{18}Br_2O_2Te$: C,36.2; H, 3.39%

Preparation of di(p.ethoxyphenyl)tellurium diiodide - The above telluride (4gms) was dissolved in carbon tetrachloride(30ml) and a slight excess of iodine solution in carbon tetrachloride was added slowly. The brown-red solid was filtered, washed with carbon tetrachloride and dried. The diiodide was recrystallized from carbon tetrachloride. Yield - 5.6gms m.p. 140°C (Lit[78]m.p. 144°C)

Preparation of di(perfluorophenyl)tellurium dihalides and di(perfluorophenyl)telluride - Cohen and his co-workers[59] have recently reported a number of possible routes to prepare di(perfluorophenyl)telluride. They described the preparation of the above telluride from direct reaction of tellurium with perfluorophenyl iodide, organomercury derivatives and organolithium derivatives. But in all these cases the yield of the telluride is very low. The author developed a new method for the preparation of the above telluride by Grignard reagent. Prefluorobromobenzene (61gms) was dissolved in diethyl ether (50ml) and the solution was added to magnesium (6.1gm) covered with dielthyl ether. The reaction started very easily and formed a dark brown solution which was refluxed for two hours. To this dark brown Grignard reagent, benzene (200ml) and ether (100ml) was added and the reaction mixture kept at 0° temp in an icebath. To the cold, well stirred solution tellurium tetrachloride (13.5gm) in benzene (200ml) was added over two hours. After the addition, the reaction mixture was refluxed for three hours, cooled and then hydrolysed with saturated ammonium chloride solution (300ml). The yellow organic layer was separated and washed with distilled water. Finally the organic solvents were removed by evaporation and crude di(perfluorophenyl) telluride was collected as a yellow solid. Yield - 25.6gm.

The crude di(perfluorophenyl)telluride (12.8gms) was dissolved in carbon tetrachloride (80ml) and added slight excess of sulphurylchloride. The white solid was filtered and the filtrate was set aside for further crystallization of the product. The white solid and the crystals from the filtrate were dissolved in Pt.ether (40-60) for recrystallization. Upon standing for a few hours, di(perfluorophenyl)tellurium dichloride was separated as white needle shaped crystals. Yield - 10gms. m.p. 201°C
Found : C,27.2; F, 35.6 calculated for $C_{12}Cl_2F_{10}Te$: C, 27.0; F,35.7%

Preparation of di(perfluorophenyl)tellurium dibromide - The crude di(perfluorophenyl)telluride (12.8gms) was dissolved in carbon tetrachloride (60ml) To this solution bromine in carbon tetrachloride (30ml) was added slowly with constant stirring. The yellow solid was filtered, washed with a solvent and dried. The di(perflourophenyl)tellurium dibromide was recrystallized from carbon tetrachloride. Yield - 13.4gms. m.p. 210°C
Found C, 24.6 calculated for $C_{12}Br_2F_{10}Te$; C, 23.3%

Reduction of di(perfluorophenyl)tellurium dibromide to pure di(perfluorophenyl)telluride. - The dibromide (5gms) was dissolved in benzene (20ml) and stirred with a saturated solution of potassium metabisulphite (40ml) for four hours at room temperature. The organic layer was separated and washed with distilled water. The evaporation of benzene afforded a yellow solid which was then crystallized from carbon tetrachloride. Yield - 2.4gms m.p. 49-50° (lit[59] m.p. 51-52°C)

Preparation of dibenzyl telluride and dibenzytellurium dihalides - The dibenzyl telluride has been described once previously[99] as a result of a reaction between dimethylphenylbenzylammonium chloride and sodium telluride. The author used the new method following the Grignard route. Benzyl bromide (44gms) was dissolved in ether (50ml) and added to magnesium (6.1gm) covered with dry ether. The reaction mixture was refluxed for 45 minutes and then cooled. Benzene (200ml) and ether (100ml) were added to it and the temperature of the content kept below 0°C. To the cold solution tellurium tetrachloride (10gms) in benzene (150ml) was added in two hours. The reaction mixture was refluxed for two hours and cooled, hydrolysed by saturated ammonium chloride solution (300ml). The yellow organic layer was separated and washed with distilled water. The organic solvents were evaporated and a yellow solid was collected. Yield - 6.8gms. When this crude product was set aside it decomposed in air[99], but in a vacuum the decomposition was very slow. The telluride decomposed to tellurium and an organic product which was shown to be dibenzyl. m.p. 52° (lit[100] m.p. 52.2°C) The telluride was used immediately for the preparation of dichloride and dibromide.

The telluride was divided into two parts. One portion (3gms) was dissolved in carbon tetrachloride (20ml) and bromine solution in CCl_4 (10ml) was added. The dark yellow solid was collected and washed with a little carbontetrachloride. The dibenzyltellurium dibromide is more stable than the telluride but it also decomposed leaving black tellurium as a residue. The compound decomposed in a melting point tube above 160°C without meing.

Found : C,33.4; H, 2.8 calculated for $C_{14}H_{14}Br_2Te$; C, 35.8,; H, 3.0%

The other portion of the telluride (3gms) was dissolved in carbon

tetrachloride (20ml) and excess of sulphuryl chloride was added. The white solid was filtered, washed with carbon tetrachloride and dried in a vaccum desiccator. The dibenzyltellurim dichloride was recrystallized from hot CCl_4. Yield - 4.1gms. m.p. 135-137°C
Found : C, 43.2; H, 3.4 calculated for $C_{14}H_{14}Cl_2Te$; C, 44.1; H, 3.7%

Preparation of tetraphenyltellurophene - This compound has been described previously[86] as a result of a reaction between 1.4 dilithio 1.2.3.4tetraphenylbutadiene (I) and tellurium tetrachloride. The compound (I) was prepared as follows. A concentrated ethereal solution of diphenylacetylene (15gms) was shaken with an excess of clean lithium shavings in a stoppered flask. After an induction period, an intense red colour developed rapidly. The reaction was exothermic, and so the reaction mixture was kept cold by a stream of air. The comp (I) precipitated during the reaction as an orange yellow powder. After two hours the yield of (I) was 70 to 85%.

To a suspension of (I) in ether (100ml), tellurium tetrachloride (8gms) in ether (200ml) was added at room temperature. The brown colour turned yellow and then greenish. The reaction mixture was poured into methylene chloride and water. After filtering the white solid, the organic layer was separated and dried on $MgSO_4$ and finally evaporated. The residue was triturated with ether, leaving tetraphenyltellurophene. Yield - 8gms m.p. 239°C (lit m.p. 236°C).

Reaction between tetraphenyltellurophene (II) and CH_3MgI - The Grignard reagent was prepared from methyl iodide (10ml) and dissolved in ether (15ml) A small amount of ethereal Grignard reagent (5ml) was taken into a flask. To this solution, tetraphenyltellurophene (1gm) in benzene (20ml) was added carefully. NO change in colour (green) nor any vigorous reaction takes place. The reaction mixture was refluxed for one hour and then hydrolysed with a saturated solution of ammonium chloride. The organic layer was separated and the solvent evaporated. The green residue was collected. m.p. 240°C.

CHAPTER 6 - RESULTS AND DISCUSSION

TABLE 4

The Infra-red and Raman Spectra of some phenyltellurium compounds below 400cm^{-1}

Ph_2TeCl_2		Ph_2TeBr_2		Ph_2TeI_2		Ph_2Te	
i.r. (cm^{-1})	Raman ($\Delta\nu$)	i.r. (cm^{-1})	Raman ($\Delta\nu$)	i.r. (cm^{-1})	Raman ($\Delta\nu$)	i.r. (cm^{-1})	Assignment
		393m	393w	393w		386m	phenyl-w
			320w				2x ν_s(TeBr)
272s	267v.s.‡	272m	274s	270m-s	268m	271s	t or (TePh)
249s	248m	258m-s	258m	256m	256m	261s	t'
				244sh		256sh	
230s	230m-s	243s	238s	233s	232m		phenyl-u
				217w			
198v.v.w.		198m-w	200m				phenyl-u'
185m	185v.v.w	186m-s*		182m	180m-w	184m	phenyl-x
				150m-w	161m	167sh	phenyl-x'
262s	267v.s‡	186m-s*		129s‡			ν_{as}(TeX)
287s	287s	159v.s	158v.v.s.		116v.v.s.		ν_s(TeX)
133m	133v.w						
							$\delta(TeX_2)$
124m	122m-w	106m	117m-w				
95w	98m	89m-w	80m	98m-w			Unassigned
	73m-w		68m				"
43w	43m		62m	54w			"
	28m		32s				"
			22s				"

‡ Asymmetric to high wave number ‡ ν_s(TeCl) + t(phenyl)

* ν_{as}(TeBr) + x(phenyl)

Infra-red and Raman Spectra of TABLE 5

(p.Tolyl)$_2$TeX$_2$

X = Cl		X = Br		X = I	
i.r.	Raman	i.r.	Raman	i.r.	Raman
381 w	388 w	383 w		394 w	
369 w	370 w	366 w		387 w	
308 m		362 w		367 w	
285 w.sh		343 w	340 m	304 w.m	
264 s	267 v.s	332 w	330 w	284 m	
255 sh		321 w	324 w	238 m	238 m
248 s	248 m	312 m.sh	308 m	205 m	203 m
239 s	244 m	299 m		193 m	
227 sh		245 m	244 m	149 v.s.br	
205 m	210 w	238 m		128 m.s	138 m
190 m.w	190 w	217 m.sh		105 ,	110 v.s
137 m		204 m	205 m	78 m	
123 m	120 w	193 m	195 m		
93 v.w		173 s	174 sh		
		167 s	167 v.s		
		157 s	158 v.s		
		93 m.s			
		82 w			

Infra-red and Raman Spectra of

TABLE 6

$(o\text{-Tolyl})_2TeX_2$

X = Cl		X = Br		X = I	
i.r.	Raman	i.r.	Raman	i.r.	Raman
385 m	384 w.m			381 w	
280 sh	280sh	395 w		260 s	109 v.v.s
275 s.br	275 s	382 w		254 m.s	
255 s	256 sh	267 s	266 s	247 m.s	
246 s.br		257 s	254 m	193 m.s	
227 s		247 s	246 m	168 w.m	
183 m	188 m	210 s	-48 sh	148 sh	
177 sh	178 w	198 s	196 m	145 s	
147 sh	144 w	184 s	182 w	139 s	
138 m	136 m	180 s		136 sh	
125 m		172 s		63 m	
	114 w	167 m.s	166 v.v.s		
	90 w	95 w			
		84 m			

TABLE 7

Infra-red and Raman spectra of

(p.methoxyphenyl)$_2$TeX$_2$

X = Cl		X = Br	
i.r.	Raman	i.r.	Raman
382 m	389 m	382 m	388 w
328 sh	383 m	329 m	326 w
317 m	359 m	314 m	
271 s.br	273 w.s	292 m.w	288 w.
247 br	253 m	227 m.s	228 w
222 s		201 m.sh	196 m
203 m		193 m.s	192 m
181 m.br	173 m	164 m.s	164 v.s
138 m.s	153 m	142 m.s.	146 s
128 m	141 m		77 m.s
117 m.s	122 m		67 m.s
	91 m		

Infra-red and Raman spectra of TABLE 8

(perfluorophenyl)$_2$TeX$_2$

X = Cl		X = Br	
i.r.	Raman	i.r.	Raman
387 m		384 m	
372		376 m	
357 w		368 w.m	
312 w		312 m	
284 s	280 m.s.	283 m	284 m
277 s	274 s	277 m	
269 s	271 s	230 m.s.	228 m
264 s	268 m	220 s	220 m
231 m	231 m	213 s	
205 s	207 m	207 s	208 m
201 s		200 sh	
194 sh		193 sh	196 w
179 w	179 w	186 sh	184 w
173 w	174 w	166 m.m	168 v.v.s
155 w	164 w	94 s	
137 w.m	152 w	86 s	
124 m	138 w	82 s	
113 w.m	126 w	71 sh.	

TABLE 9

Infra-red and Raman spectra of
(p.ethoxyphenyl)$_2$TeX$_2$

X = Cl		X = Br		X = I		(p.ethoxyphenyl)$_2$Te
i.r.	Raman	i.r.	Raman	i.r.	Raman	i.r.
382 s		383 s		382 s		382 s
378 s		329 s		378 s		370 w
364 w		318 s		365 w		324 m
335 m		262 m		310 m		308 s
310 m		234 m		210 m		231 w
274 s		217 m		198 w		206 s
263 s		185 m	180 m	170 m	162 w	174 v.s
236 s.br		157 m	168 s	138 w	143 w	169 v.s
330 s				114 w	111 s	163 v.s
210 m						132 s
143 w						128 sh
138 w						102 m

TABLE 11

Conductivity measurement of diphenyl tellurium dibromide and diiodide in methyl cyanide

Compound	Conductivity
Ph$_2$TeBr$_2$	8.1 Ohm^{-1}cm^{2}Mole^{-1}
Ph$_2$TeI$_2$	11.56 " " "

TABLE 10

Tellurium Halogen Vibrations (i.r.)

R in R_2TeX_2	X = Cl	X = Br	X = I	
C_6H_5-	287	159	116‡	s
	262	196	129	as
p-Ch_3.C_6H_4-	264	167,157	110‡	s
	248	173	149	as
o-CH_3.C_6H_4-	275	166	109‡	s
	255*	172	148sh,145	as
p-CH_3O.C_6H_4-	271	164	-	s
	247	193	-	as
C_6F_5-	269	168‡	-	s
	264	184	-	as

* mixed with R modes

‡ = from Raman spectrum

ν_s = Symmetric mode

ν_{as} = Asymmetric mode

s = Strong

m = Medium

w = Weak

sh = Shoulder

br = Broad

_ = ν(Te - X)

B. DISCUSSION

Compounds of the tellurium with simple organic groups such as phenyl, p-tolyl, o-tolyl, p-methoxyphenyl, p-ethoxyphenyl were prepared. Also some new compounds with perfluorobenzene and benzyl groups have been prepared to invesigate the possible change, if there is any, in the structure of the organotellurium compound. The X-ray analysis of diphenyltellurium dibromide[91] showed that the molecule has a ψ-trigonal bipyramidal type of structure with the halogens at axial positions and the two phenyl groups at the equatorial positions along with one pair of unshared electron. The observed Te-Br bond distance of 2.682A^0 was longer than the sum of the single covalent radii for these atoms. Also the observed bond angle Br-Te-Be of 178^0 agreed well with the values of 177.5 ± 1.0^0 and 177.0± 1.0^0 found for Cl-Se-Cl and Br-Se-Br respectively in the di(p.tolyl) selenium dihalides[101]. In all three molecules the direction of the deviation is such that the halogen atoms are moved slightly away from the phenyl groups. The infra-red spectra of the simple organotellurium compounds have been reported and assignments of phenyl-tellurium (Ph-Te) stretching frequencies have been discussed[93].

The far infra-red and Raman spectra of the diphenyltellurium dihalides and diphenyl telluride are tabulated in table-4. The assignment of tellurium-phenyl group vibrations offered follow Wiffen's[102] notation for monosubstituted benzenes. Wiffen reported the infra-red and Raman spectra of monosubstituted benzenes in terms of their symmetry class and each vibration has been given a notation. Considering monosubstituted benzene in symmetry terms, it belongs to C_{2v} symmetry and it has 11 A_1 class fundamental modes, $10B_1$, $3A_2$ and $6B_2$ modes. He reported all 30 vibrations of the monosubstituted benzene $X-C_6H_5$ (X = F,Cl,Br and I). Looking at the spectra in the region of X-sensitive modes, it appears that as the atomic weight of the substituent increases, the particular X-sensitive mode vibration decreases to lower wave numbers, e.g. the X-sensitive 'x' modes of the monosubstituted benzenes appeared at 241, 196,181 and 161 cm^{-1} in the Raman spectra of X = F,Cl,Br and I respectively. Similarly all the six X-sensitive modes have been reported in Raman as well as in infra-red spectra. In the case of iodobenzene[102] the X-sensitive infra-red and Raman bands were reported as follows:

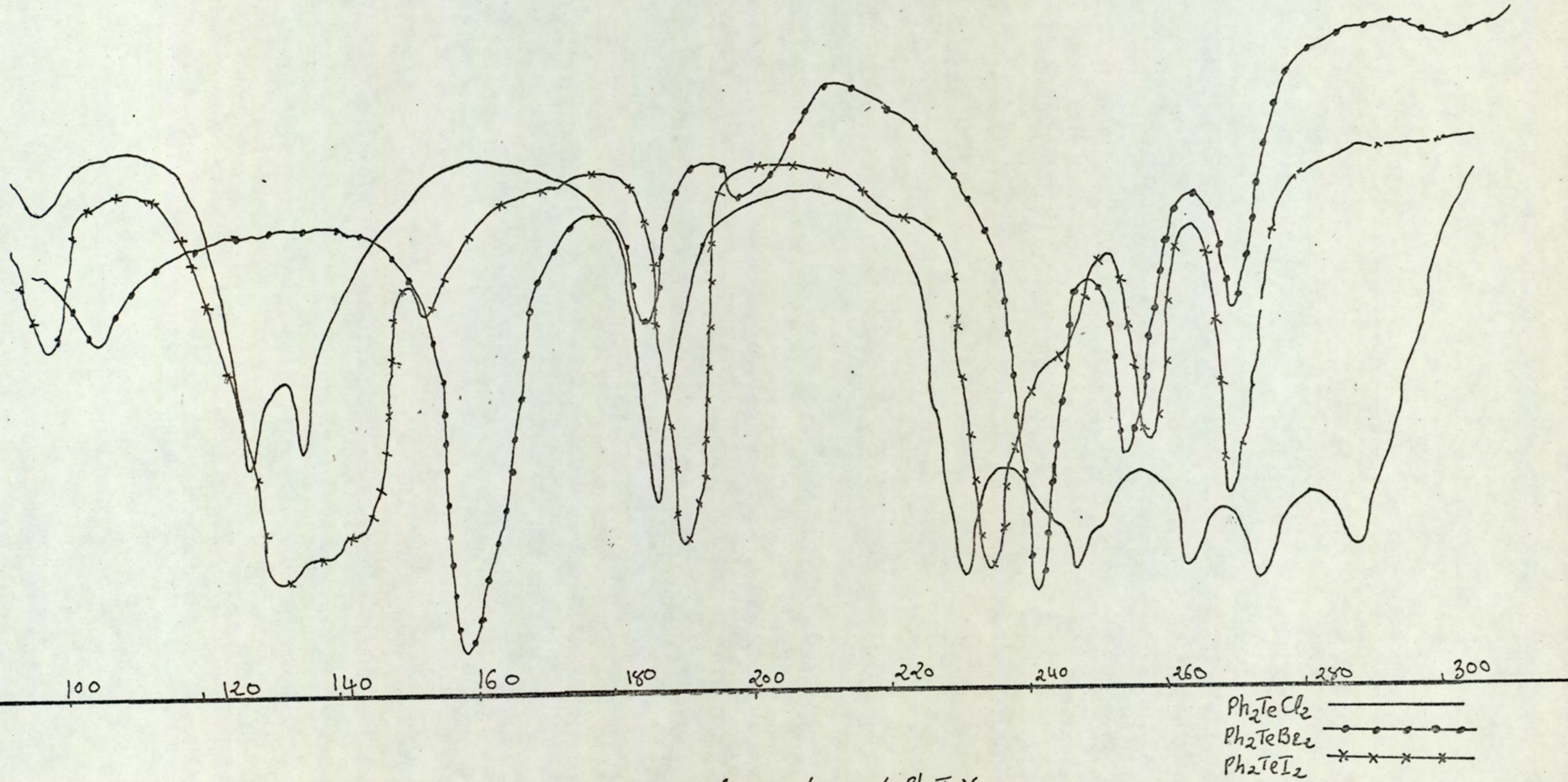
X-sensitive mode		't'	'U'	'y'	'x'
Vibration in cm^{-1}	I.R.			448	-
	Raman	266	220	450	166

Some of the bands in the spectrum of diorganotellurium dihalides could be designated 'metal-phenyl stretching' modes as is common practice in organotin chemistry. Considering a diphenytellurium dihalide as a monosubstituted benzene $Te-C_6H_5$, the X-sensitive (X = Te) "t" and "t'" modes occur between 249 and 277 cm^{-1}. One earlier paper[93] described the tellurium-phenyl stretching frequency between 455 and 487cm^{-1} in which region the X-sensitive "y" mode is expected. In organotin chemistry it is generally accepted[103] that the "t" mode of phenyl tin compounds occurs between 250 and 270 cm^{-1} which is very close to "t" mode of iodobenzene at 266cm^{-1} in the Raman spectra. It is known that the X-sensitive modes of monosubstituted benzenes depend upon the masses of the substituent. The mass of iodine, tin and tellurium are similar and also the oxidation state of tellurium and tin in these compounds is four, so the comparison of organotin compounds with organotellurium compounds may be justified.

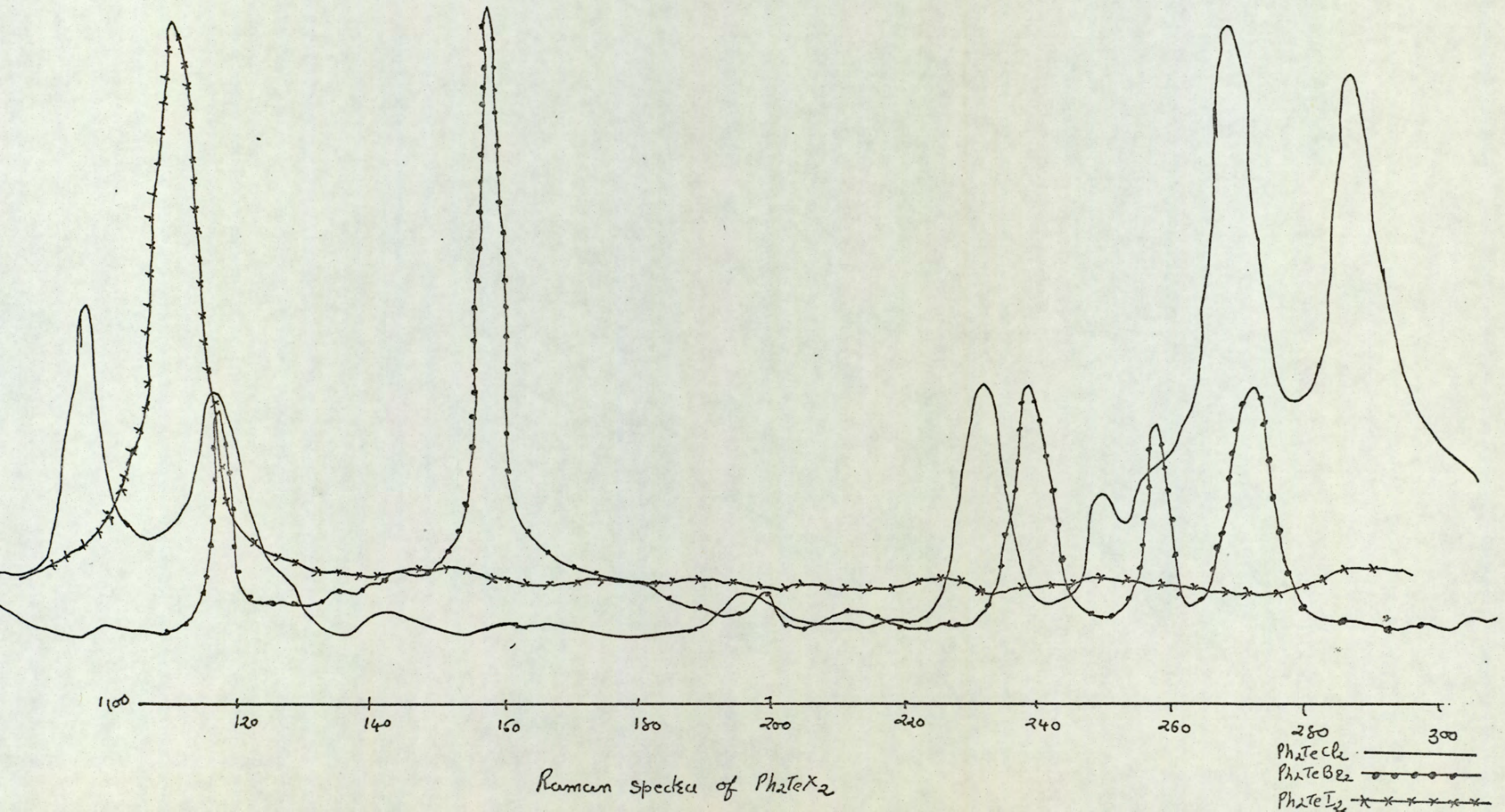
The X-sensitive modes of the diphenyltellurium dihalides should occur in the region in which the same modes occur for iodobenzene[102]. So all other X-sensitive modes "x" and "u" could be assigned for the diphenyltelluriumdihalides.

In contrast to the comparable phenyl vibrations for Ph_2SnX_2[104,105] (Ph = phenyl) and Ph_2TeX_2 the long tellurium to halogen bonds in Ph_2TeX_2 leads to a dramatic lowering of the metal halogen stretching frequencies in the tellurium series. The tellurium halogen modes assigned in table-4 require some comment. The Raman band at $\Delta\nu = 267cm^{-1}$ is very intense and thus could be assigned as ν_s(Te-Cl). However, in the spectrum of iodobenzene the X-sensitive "t" mode occurs at 266cm^{1-} and the mass of tellurium is similar to iodine, it is clearly a composite band with the phenyl "t" mode being co-incident and contributing to the observed intensity in the spectrum of Ph_2TeCl_2. The examination of more complex diaryltellurium dihalides (table-10) suggests that generally ν_s(Te-Cl) mode occurs at higher frequency than those for ν_{as}(Te-Cl) mode. Hayward and Hendra[89] reported the detailed Raman and infra-red spectra of dimethyltellurium dichloride and they also assigned tellurium-chlorine stretching frequencies in the same manner. Thus the band at 287cm^{-1} in both infra-red and Raman spectra could be assigned as ν_s(Te-Cl) and the band at 262cm^{-1} in infra-red and 267cm^{-1} in the Raman spectra could be assigned as ν_{as}(Te-Cl) mode. The very strong band at 267cm^{-1} in the Raman spectrum could be a composite band of ν_{as}(Te-Cl) plus phenyl "t" mode.

Although assignment's of telluriumchlorine stretching frequencies could be compared with the Me_2TeCl_2 it was felt that diphenytellurium dibromide and diiodide produce some difficulty in the assignment of tellurium



Infra-red Spectra of Ph_2TeX_2



Raman spectra of Ph_2TeX_2

bromine and iodine stretching frequencies. The tellurium bromine stretching frequency might be expected at 180cm^{-1} by comparison with the data for Me_2TeBr_2, however the phenyl 'x' modes are also expected in this region. The infra-red spectrum of Ph_2TeBr_2 shows a band of enhanced intensity at 186cm^{-1} which could be assigned as a mixture of -phenyl `x' mode and ν_{as}(Te-Br) mode. The Raman spectrum does not show any band in the similar region. Hayward and Hendra[89] made the remark that for the series Me_2TeX_2 asymmetric metal-halogen stretching frequency was of no more than medium to weak intensity; this suggestion appears more true for Ph_2TeBr_2 and Ph_2TeI_2. The Raman spectrum of Ph_2TeBr_2 shows the tellurium phenyl 'x' mode to be only weakly Raman active. It shows a very intense band at 158cm^{-1} (fig 6.1) so intense that it appears that there must be some preresonance Raman enhancement. So the strongest band in the Raman spectrum 158cm^{-1} of Ph_2TeBr_2 is assigned as ν_s(Te-Br), similar assignment is made for the comparatively strong band at 159cm^{-1} in the infra-red spectrum. As was suggested by Hayward and Hendra[89] that a weak or medium weak band could be assigned as ν_{as}(Te-X), the medium strong infra-red absorption at 186cm^{-1} is assigned as a mixture of ν_{as}(Te-Br) and phenyl 'x' mode. It appeared from the spectra that the symmetric tellurium-bromine stretching frequency occurs at a lower wave number than ν_{as}(Te-Br). Hayward and Hendra made similar assignments for Me_2TeBr_2. The weak band at $\Delta\nu$ = 320cm^{-1} in the Raman spectrum of the Ph_2TeBr_2 is assigned as 2 x ν_s(Te-Br).

The Raman spectrum of Ph_2TeI_2 is dominated by an extremely intense band at $\Delta\nu$ = 116cm^{-1}. The figure 6-2 illustrates the diffuse reflectance spectra of the Ph_2TeBr_2 and Ph_2TeI_2. In the case of Ph_2TeI_2, the exciting line (6328A^0, 15803cm^{-1}) is coincident with the longer wavelength section of the first electronic absorption band resulting in considerable

Figure 6-1

Laser Raman Spectrum of Ph_2TeBr_2

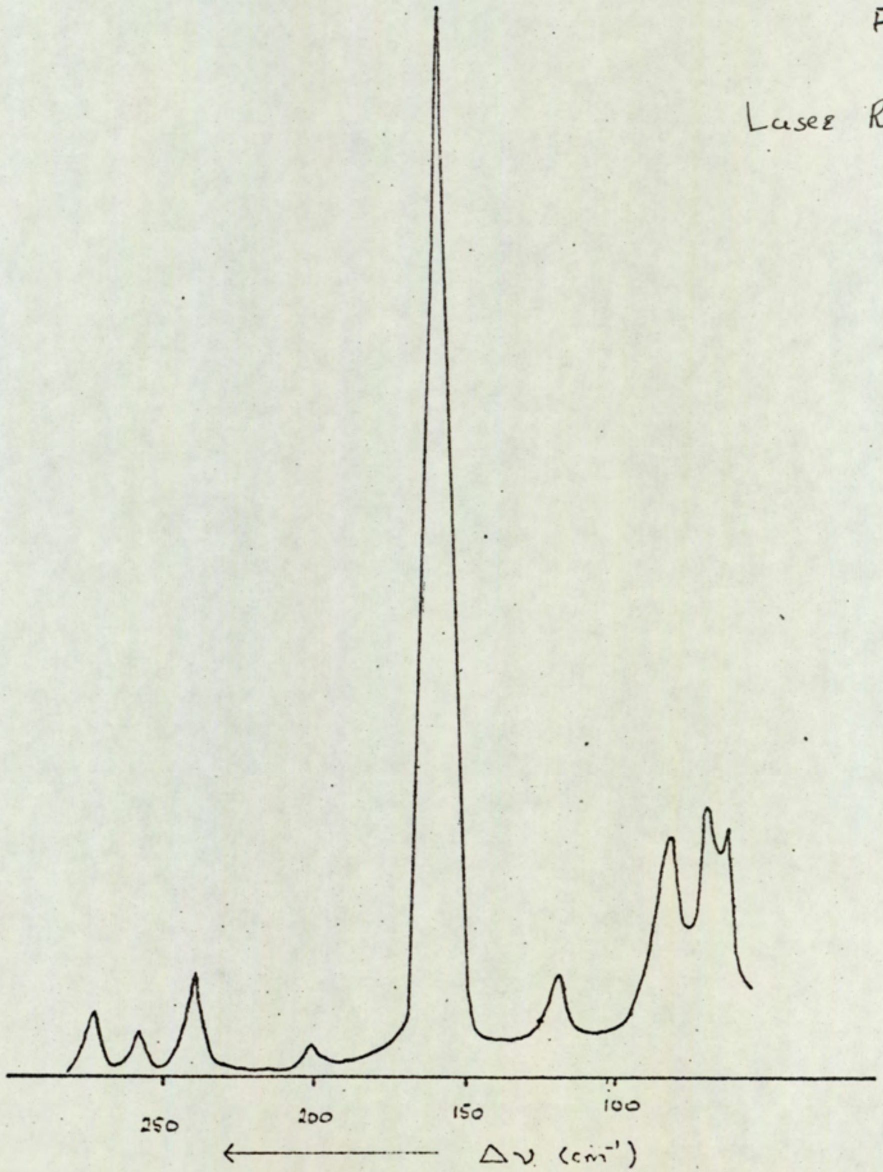
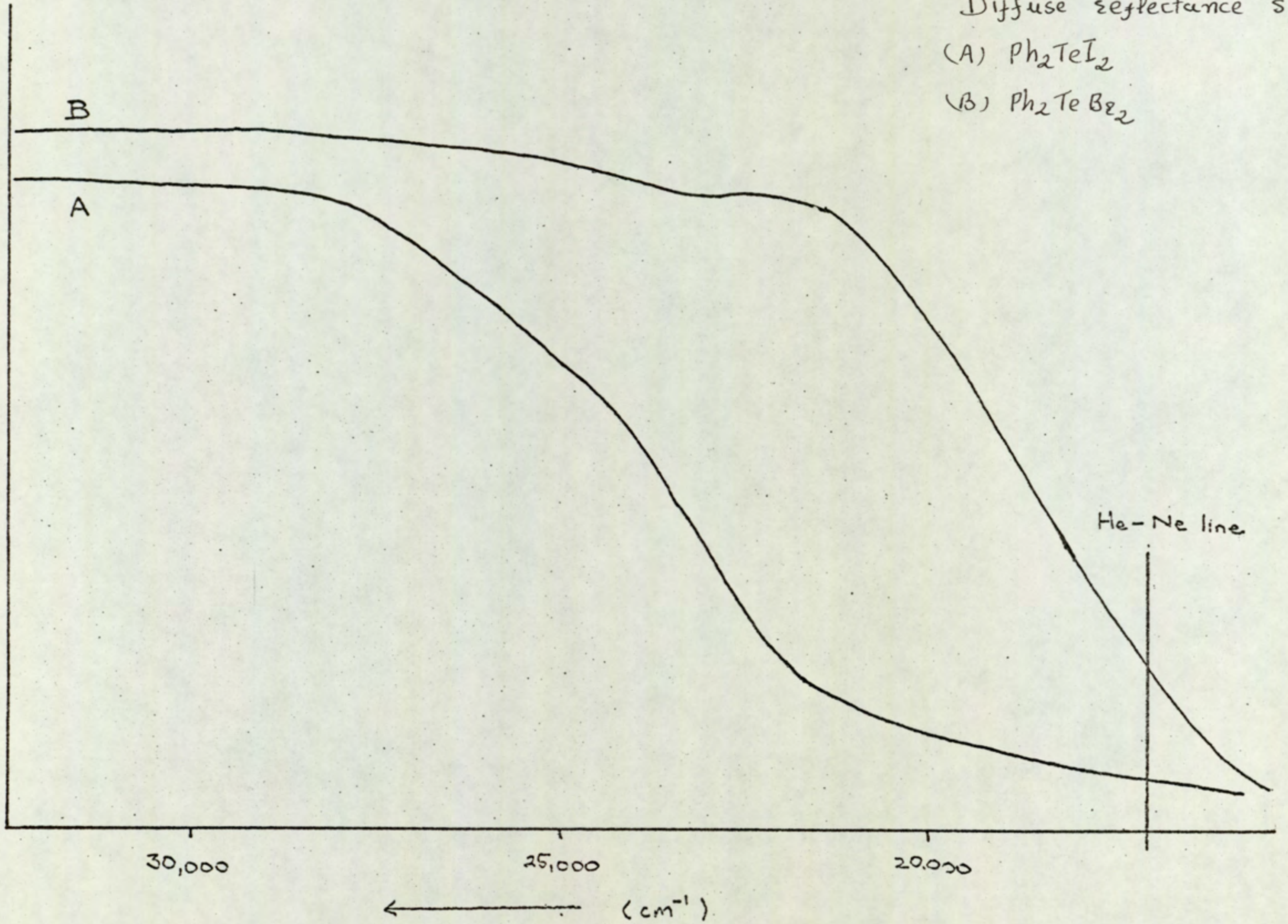


Figure 6.2

Diffuse reflectance spectra of
(A) Ph_2TeI_2
(B) Ph_2TeBr_2



enhancement. The assignment of ν_{as}(Te-I) and ν_s(Te-I) from the low frequency vibrational modes in the Ph_2TeI_2 are not unreasonable when compared with those accepted for Me_2TeI_2[89], however in the case of Ph_2TeI_2 the Raman band at $\Delta\nu$= 116cm^{-1} has no infra-red counterpart. It was found difficult to assign infra-red and Raman bands below 100cm^{-1} since this region is likely to include lattice vibrations. The Te-I symmetic mode is assigned at 116cm^{-1} in the Raman spectrum but the infra-red counterpart does not appear in the same region. The Te-I asymmetric mode is assigned at a higher frequency at 129cm^{-1} in the infra-red spectrum only. The X-ray powder photographs were similar which suggests similar structures.

The far infra-red and Raman spectra of the series of other diaryltellurium dihalides have been measured. Although the pattern of the general profile of the spectra were similar, some frequency differences were observed as the aryl group changes. The tellurium halogen stretching vibrations are assigned. In the Raman spectra, here too the dibromides and diiodides again gave evidence of preresonance and resonance Raman effect with the result that the symmetric modes are the dominant in the spectra and in the case of di(p.tolyl)tellurium diiodide only one band was observed in the low frequency Raman spectrum (table 5). The assignments of the tellurium-chlorine stretching frequencies ν(Tl-Cl) were made by the comparison of infra-red and Raman spectra of the corresponding dibromide and diiodide.The two bands selected for Te-Cl stretching frequencies in the infra-red spectrum, the one at the higher frequency has the more intense Raman counterpart and so assigned to the symmetric mode. The asymmetric mode is assigned at lower frequencies with a medium intensity. The assignment of ν(Te-Br) and ν(Te-I) produce difficulty in this series, but here too the Raman spectra were found to be very useful. So like the diphenyltelluriumdibromide and diiodide, the assignment of tellurium-halogen (halogen = Br & I) stretching frequencies were made. In the Raman spectra the band at a lower frequency with higher intensity is assigned for symmetric mode, while the band at higher frequencies with relatively low intensity in the infra-red spectrum is assigned for asymmetric mode. For the dichloro compounds the bands between 140 and $120cm^{-1}$ may be assigned as δ(TeX) mode.

The molecular structure of the series diaryltellurium dihalides does not differ greatly even if the substituent on the phenyl group changes. The data from the (table 5-10)show clear evidence of this and so it must be considered that in all cases the halogen atoms occupy the axial positions in a ψ-trigonal bipyramid. The tellurium halogen stretching frequencies vary slightly as a function of the substituent in the aryl group. But in the case of dichlorides and dibromides the bands appear in a rich region of the spectrum, and could not be considered to be pure vibrations in view of the low symmetry of the molecular structure.

In the molecular structure of diaryltelluriumdihalides if the phenyl groups are replaced by a more electronegative group such as perfluorobenzene, one would expect a change in the aryl group position at an equatorial position. So di(perfluorophenyl)tellurium dibromide and dichloride were prepared. But the general profile of the spectra of the above compounds were similar to those of corresponding diphenyl tellurium dihalides (table 8). It appeared from the spectroscopic evidence that the equatorial positions of the aryl group did not change considerably even after the introduction of $(C_6F_5^-)$ group in the molecular structure.

The infra-red and Raman spectra of the dibenzyltellurium dihalides (halide =

Cl,Br) were not obtained because of their low stability. The ^{1}H n.m.r. spectra of the freshly prepared solution of dibenzyltellurium dichloride was obtained. The spectrum did not give much information about the coupling of the methylene group with ^{125}Te, because of the low solubility of the compound. The dibromide is very unstable compared to dichloride and the solubility is so low that the ^{1}H n.m.r. spectrum was not possible. The spectrum shows very weak bands but it would be dangerous to assign those bands for a coupling constant as it could arise from spinning side bands.

An attempt was made to prepare a telluroylid, but the reaction did not work as it was hoped.

CHAPTER 7

Some possible uses of diaryltellurides as debrominating agents - stoichiometrically and catalytically.

A. INTRODUCTION : It is known that diphenyltelluride reacts with dibromo organic compounds such as dibromoethane and dibromostilbene to form diphenyl tellurium dibromide and unsaturated organic compounds.[106] One particular monobromo organic compound such as allyl bromide reacted with diphenyltelluride to form diphenyltellurium dibromide and probably diallyl[106].

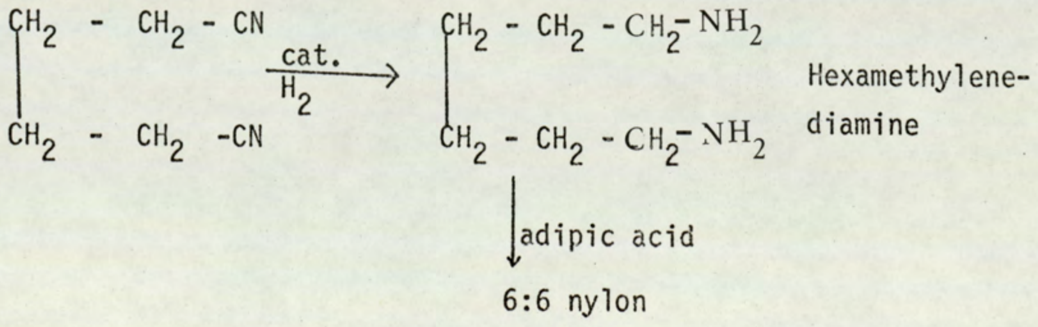
$$2CH_2 = CH - CH_2 - Br + Ph_2Te \longrightarrow Ph_2TeBr_2 + 2(CH_2 = CH - \dot{C}H_2)$$

or

$$2(\dot{C}H_2 - CH = CH_2)$$

The resonance stabilisation of the allyl intermediate may provide the kinetic and thermodynamic driving force for this reaction.

In the preparation of 6:6 nylon adipontrile is used as an intermediate compound



$$\begin{matrix} CH_2 - CH_2 - CN \\ | \\ CH_2 - CH_2 - CN \end{matrix} \xrightarrow[H_2]{cat.} \begin{matrix} CH_2 - CH_2 - CH_2 - NH_2 \\ | \\ CH_2 - CH_2 - CH_2 - NH_2 \end{matrix} \text{ Hexamethylene-diamine} \xrightarrow{\text{adipic acid}} \text{6:6 nylon}$$

Adiponitrile may be considered to be a 2 x 3 carbon fragment molecule and if one were to take a similar 3 carbon fragment molecule and successfully dimerise it, adiponitrile would be obtained.

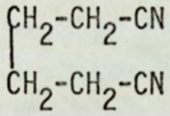
3 - bromopropionitrile has a similar 3 carbon fragment.

$$Br - CH_2 - CH_2 - CN$$

If this molecule reacted with diphenyltelluride and was debrominated, the radical $\dot{C}H_2 - CH_2 - CN$ might dimerise to form adiponitrile. If this happened then with the help of diphenyltelluride adiponitrile could be obtained from 3-bromopropionitrile.

$$2Br - CH_2 - CH_2 - CN + Ph_2Te \qquad Ph_2TeBr_2 + 2(\dot{C}H_2\text{-}CH_2\text{-}CN)$$

on dimerisation



$$\begin{array}{l} CH_2\text{-}CH_2\text{-}CN \\ | \\ CH_2\text{-}CH_2\text{-}CN \end{array}$$

Some reactions were therefore carried out to investigate, the reaction between diphenyltelluride and 3-bromopropionitrile and 2-bromoacrylonitrile to produce similar 2 x 3 carbon system, which could be used in the preparation of 6:6 nylon. The better compound 2-bromoacrylonitrile was selected as a relatively readily available material which might afford a resonance stabilised intermediate and hence drive the debromination reaction to completion.

Diphenyltelluride reacted with dibromo organic compounds to form debrominated unsaturated compounds.

$$Br - CH_2 - CH_2 - Br + Ph_2Te \qquad Ph_2TeBr_2 + CH_2 = CH_2$$

Also it is known that diphenyltellurium dihalide can be reduced by ordinary reducing agents like Na_2S, $SnCl_2$, $K_2S_2O_5$ etc., to form diphenyl telluride.

$$Ph_2TeBr_2 + Na_2S \longrightarrow Ph_2Te + 2NaBr + S$$

This mechanism leads to the investigation of the continuous use of diaryltelluride as a dehalogenating agent in the presence of a reducing agent

$$\begin{tikzcd}
Ph_2Te + Br - CH_2 - CH_2 - Br \arrow[r] & CH_2 = CH_2 \\
 & + \\
S + 2NaBr + Ph_2Te \arrow[uu, "\text{recycle}"'] & Ph_2TeBr_2 \arrow[l, "Na_2S"']
\end{tikzcd}$$

Attempts were made to investigate possible catalytic dehalogenation of dibromo organic compounds with the use of diphenyl telluride in the presence of different reducing agents.

B. EXPERIMENTAL

Reaction between diphenyltelluride and 3-bromopropionitrile - In a 100ml. round bottomed flask 3-bromopropionitrile (10.3gms) and diphenyltelluride (0.754gms) were refluxed for 2 hours. The mixture was then cooled and allowed to crystallize. After a few hours only a few yellow crystals were obtained. The yellow crystals were separated which were sufficient to run infra-red spectra and m.p. measurement. The m.p. (197^oC) and also the infra-red spectrum was similar to Ph_2TeBr_2. This indicated that the debromination has taken place to some extent but no further solid was obtained from the residue even after evaporation of 3-bromopropionitrile, indicating that the desired dimerisation did not take place.

Another attempt was made taking a stoichiometric amount of both the reagent in a sealed tube at a higher temperature. So 3-bromopropionitrile (1.4gms) and diphenyl telluride (1.35gms) were taken into a small tube and sealed. The sealed tube was heated at 150^{0}C for 12 hours. Both the compounds were decomposed to give a brown substance which was insoluble in organic solvent and also in water. The infra-red spectrum did not show any organic group vibrations.

At a lower temperature (at 110^{0}C) the similar mixture in a sealed tube afforded only a little amount of yellow crystals but again no further solid was obtained. So the desired debromodimerisation was unsuccessful.

Preparation of dibromopropionitrile - The dibromopropionitrile was prepared as the method described by Moyer and his co-workers[107]. To a one litre three necked flask equiped with magnetic stirrer, bromine addition funnel, thermometer and reflux condenser, was added acrylonitrile (318gms). The flask was irradiated with 200 watt incandescent light bulb and 6 mole of bromine (960gms) was added dropwise over a 2 hour period. The temperature was readily maintained at 25^{0}C. The product yield was 1277 gms of orange liquid, 2:3 dibromopropionitrile.

Preparation of 2-bromoacrylonitrile[108] - 2.3 dibromopropionitrile (25gms) was treated with potassium cyanide in chloroform (200ml) in the presence of a few drops of water and hydroquinone (1gm). The mixture was boiled for 5 minutes. The residue was filtered and dried over $CaCl_2$. The solution was then distilled giving 2-bromoacrylonitrile as a pale yellow oil : B.P.116^{0}. Mass spectra confirmed the purity of the compound.

Reaction between 2-bromoacrylonitrile and diphenyl telluride - 2-bromoacrylonitrile (1.32gm) and diphenyl telluride (1.4gm) was taken into a sealed tube and heated at 110°C for 10 hours. There was no change in the colour. The mixture was allowed to crystallize but no crystals were formed. It seems that no reaction had taken place.

The same amount of diphenyl telluride and 2-bromoacrylonitrile was taken into another sealed tube, and heated at 130°C for 8 hours. The colour of the mixture changed from yellow to black. The tube was then broken and the contents extracted with chloroform. The insoluble black compound did not show organic material but it gave a ν(CN) stretching frequency at 2230 cm^{-1}. Also the sodium fusion test indicates the presence of tellurium and nitrogen. The filtrate was allowed to crystallize and a white solid was collected. The infra-red spectra did not show nitrile vibration and the sodium fusion test indicates the presence of bromine but no tellurium, nitrogen. The m.p. of the comp. is very high (255-260°).

Investigation of catalytic use of diphenyl telluride in the dehalogenation if dihalo organic compounds. - Two separate experiments were carried out. In one dibromoethane (20gms) and diphenyl telluride (1.2gms) were heated for two hours. During this time the diphenyltelluride would react with dibromoethane to form ethylene and diphenyltellurium dibromide. After 2 hours hydrated sodium sulphide was added to the warm solution and reflux for another three hours. But after 30 minutes a white precipitate was formed which increased in an hour. After 3 hours the organic layer was extracted with benzene. The white material was insoluble in water and most of the organic solvent. Although the compound was not characterized it might be a long chained compound such as $(-CH_2-CH_2-S-)_n$.

In another experiment dibromoethane (20gms) was heated with hydrated sodium sulphide for 2½ hours. The same white compound was formed during the reaction.

Reaction between dibromoethane and diphenyl telluride in the presence of potassium metabisulphite - Dibromoethane (20gms) was refluxed with diphenyl telluride (1.2gms) for 2 hours. Then a saturated solution of potassium metabisulphite (20ml) was added dropwise and again the mixture was refluxed for another 2 hours. The mixture then cooled and organic compounds were recovered with benzene. The clear aqueous solution of potassium metabisulphite was decomposed with dilute nitric acid and then heated for 10 minutes. To the hot solution silver nitrate solution was added in excess.

The weight of silver bromide was found only to correspond to the slight reduction of diphenyltelluriumdibromide by potassium metalbisulphite. In the organic layer mixture of diphenyltelluride and diphenyltellurium dibromide was found.

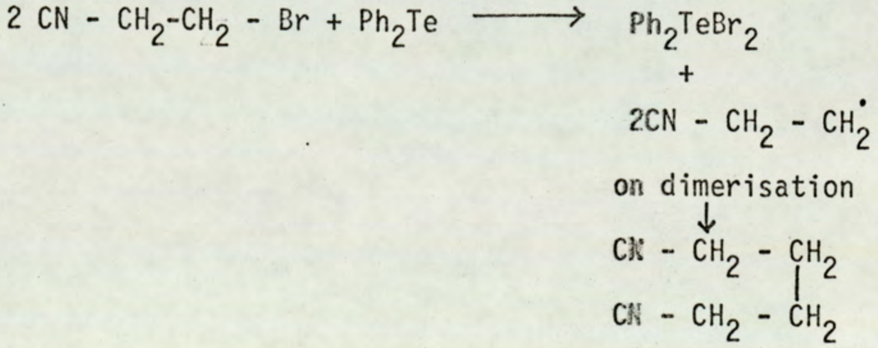
Similar results were obtained when sodiumborohydide was used as an intermediate reducing agent.

Reaction between stilbenedibromide and diphenyl telluride in the presence of potassium metabisulphite. - Stilbenedibromide (2.4gms) and diphenyl telluride (1.2gms) were dissolved in p-xylene and refluxed for 3-hours. During this time diphenyl tellurium dibromide would have formed. To the warm solution a saturated solution of potassium metabisulphite was added carefully and refluxed for another 3 hours. The reaction mixture was cooled and potassium metabisulphite solution was separated and boiled for 30 minutes. Dilute nitric acid was then added to decompose the sulphite and then silver nitrate solution was added. The weight of the silver bromide was found only to be 0.15gms which was very much less than the corresponding bromide if all the diphenyltellurium dibromide had been reduced.

It was not considered worthwhile to attempt the reaction in the presence of sodium borohydride because sodium borohydride reacted with stilbenedibromide to debrominate the compound in 15 minutes. The diphenyltelluride debrominated stilbenedibromide in about 2 hours so the catalytic use of diphenyl telluride was not feasible in this instance.

C. DISCUSSION

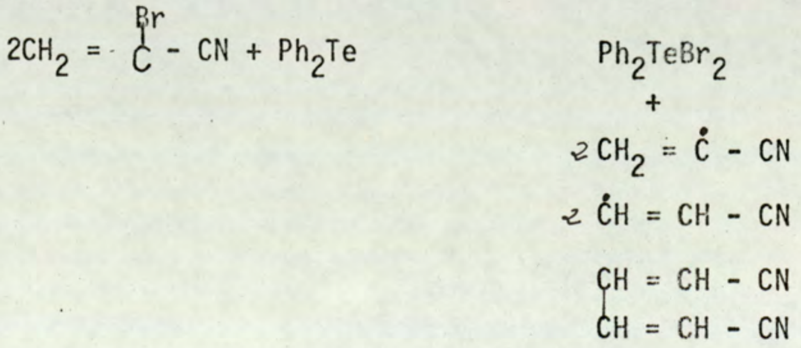
As described in the introduction allylbromide reacted with diphenyl telluride to form diphenyltellurium dibromide and probably diallyl[106]. This reaction leads to investigate the possible use of diphenyltelluride as a debrominating agent of monobromonitrile compounds. So if diphenyltelluride reacted with 3-bromopropionitrile after the debromination, the active radical might dimerise to form dinitrile i.e. adiponitrile.



$$2\ CN-CH_2-CH_2-Br + Ph_2Te \longrightarrow \begin{array}{c} Ph_2TeBr_2 \\ + \\ 2CN-CH_2-\dot{C}H_2 \\ \text{on dimerisation} \\ \downarrow \\ \begin{array}{l} CN-CH_2-CH_2 \\ \qquad\qquad\quad | \\ CN-CH_2-CH_2 \end{array} \end{array}$$

This adiponitrile used as an intermediate compound in the preparation of 6:6 nylon, but the experimental results show that the reaction did not take place as was hoped. Although at a higher temperature the reaction has occured but the organic compound and diphenyltelluride decomposed to form a brown compound which was insoluble in organic solvents and the infra-red spectra did not show any organic group vibrations. This compound might be a polymer of 3-bromoacrylo nitrile itself or similar compounds. At some stage diphenyltellurium dibromide was produced but the amount was so low that the other debrominated compound would not be isolated even after the evaporation of 3-bromoacrylonitrile. So the desired dimeric product was not obtained with diphenyl telluride.

Another attempt was made using similar 3-carbon fragment systems such as 2-bromoacrylonitrile. This compound was prepared from acrylonitrile. If from acrylonitrile a similar dinitrile compound such as muconic dinitrile could be prepared with the help of diphenyl telluride, the process of nylon preparation would be more economical. 3-bromoacrylonitrile is a possible best isomer, by the reaction can be started but as the synthesis of 3-bromoacrylonitrile is difficult and the time did not permit to synthesise it, 2-bromoacrylonitrile, which is easily prepared from acrylonitrile was used with diphenyl telluride. The compound was chosen with the hope that after the debromination, if protonic migration occur , the resonance stabilization with kinetic or thermodynamic driving force might lead to the formation of dimeric compound such as muconic dinitrile.



$$2CH_2 = \overset{\overset{Br}{|}}{C} - CN + Ph_2Te \qquad Ph_2TeBr_2 + 2CH_2 = \dot{C} - CN$$

$$2\dot{C}H = CH - CN$$

$$\begin{array}{l} CH = CH - CN \\ | \\ CH = CH - CN \end{array}$$

Again the experiment showed that at a lower temperature the reaction between diphenyltelluride and 2-bromoacrylonitrile did not proceed and at a higher temperature both the compounds decomposed and two substances were isolated. The sodium fusion test of insoluble black materials shows the presence of tellurium and nitrogen and the infra-red spectrum showed a band at $2230cm^{-1}$ which corresponds to $\nu(CN)$. These results indicate that the material might be tellurium dicyanide. The other compound has a very high m.p. (255-260) and it did not show $\nu(CN)$ absorption in the infra-red spectrum. So the possible debromodimerisation of 2-bromoacrylonitrile by diphenyl telluride was not successful.

The reaction between diphenyl telluride and dibromoethane in the presence of a cheap reducing agent such as Na_2S affords only one white compound which could be $(-CH_2-CH_2-S-)_n$. The catalytic debromination did not proceed. With another reducing agent, potassium metabisulphite, the reaction between dibromoethane and the reducing agent did not take place but in the presence of dibromoethane the reduction of diphenyltellurium dibromide might not have occur and so the catalytic debromination of dibromoethane was unsuccessful. Dibromostilbene can be debrominated by diphenyl telluride[106] but the experiment showed that in the presence of dibromostilbene the reduction of diphenyltellurium dibromide to telluride by $K_2S_2O_5$ might not occur. Sodium borohydride was not considered as an intermediate reducing agent because it reacted with dibromostilbene to produce stilbene and the reaction is faster than with the telluride. King and Allbutt[109] reported the reaction of sodium borohydride with many dibromo organic compounds. So the catalytic use of diphenyl telluride as a debrominating agent in the presence of a reducing agent was unsuccessful.

Although the reactions were unsuccessful, the use of organometallic compounds must be considered very seriously. The author feels that the future worker in this field must consider the use of organometallic compounds together with the more academic chemistry.

REFERENCES

1. T.J.Rowland & J.Phillip Bromberg - J.Chem.Phys. 29,626,(1958).

2. R. Freeman, P.H.Gasser & R.E.Richards - Mole.Phys. 2,301,(1959).

3. S.Hafner & N.H.Nachtrieb - J.Chem.Phys. 40,2891,(1964).

4. G. Sutton - Aust.J.Sci.Res. A4,654,(1951).

5. G. Sutton - Aust.J.Chem. 11,120,(1958).

6. F.Ya.Kul'ba et.al. - Russ.J.Inorg.Chem. 8,468,(1963).

7. R.J.Meyer - Z.Anorg.Chem. 24,321,(1900).

8. K.Renz - Ber. 35,1118,(1902).

9. W.Krause & Gresse - Ber 59,1712,(1926).

10. F.Ya.Kul'ba et.al. - Russ.J.Inorg.Chem. 8,1217,(1963).

11. F.A.Cotton, B.F.G.Johnson & R.M.Wing - Inorg.Chem 4,502,(1965).

12. W.J.Geary - Co-ord. Chem.Revs. 7,110,(1971).

13. W.R.McWhinnie - J.Chem.Soc.(A) 889, (1966).

14. T.G.Spiro - Inorg.Chem. 7,640,(1968).
    - ibid. 4,1290,(1965).

15. R.A.Walton - Inorg.Chem. 7,640,(1968).

16. R.A.Walton - J.Inorg.Nucl.Chem. 32,2875,(1970).

17. R.A.Walton - J.Chem.Soc.(A) 1485,(1967).
    - ibid. 61,(1969).

18. D.M.Adams, A.J.Carty & D.G.Tuck - J.Chem.Soc.(A) 162,(1968).

19. A.J.Carty - Can.J.Chem. 46,3779,(1968).

20. R.Restivo & G.J.Palenic - Chem.Comm. 867,(1969).

21. L.A.Woodward & M.J.Tayler - J.Chem.Soc. 4473, (1960).

22. F.A.Kul'ba,V.E.Mironov & L.A.Ananeva - Russ.J.Inorg.Chem. 8,1219,(1963).

23. D.P.Stevenson & J.Schomaker - J.Am.Chem.Soc. 62,1263,(1940).

24. A.A.Schilt & R.C.Taylor - J. Inorg.Nucl.Chem. 9,211,(1959).

25. F.A.Kulba,N.G.Yaraslvanskii. et.al.- Russ.J.Inorg.Chem. 13,79,(1968).

26. J.E.Reynolds - J.Chem.Soc. 53,857,(1888).

27. A.Rosenheim & W.Loewenstamn - Z.Anorg.Allgen.Chem.34,72,(1903).

28. G.Pfrepper - Z.Anorg.Allgen.Chem. 347,160,(1966).

29. C.Mahr & H.O. - Ann.Chem.Liefigs 542,44,(1939).

30. L.P.McHutton & M.J.Soulal - J.Chem.Soc. 4095,(1953).

31. E.G.Cox,A.J.Shorter & W.Wardlaw - J.Chem.Soc. 1886,(1938).

32. J.C.A.Boeyens & F.H.Herbstein - Inorg.Chem. 6,1408,(1967).

33. J.P.Wibaut & G.L.C.LaBastide - Rec.Trav.Chim. 52,493,(1933).

34. S.Buffagni & T.M.Dunn - J.Chem.Soc. 5105,(1961).

35. Y.Pocker - J.Chem.Soc. 240,(1958).

36. A.I.Vogel - Practical Organic Chem. Longmans London a) p.171 b)p.407.

37. G.C. Kulasingam - Ph.D.thesis Uni. of London.(1967).

38. A.F.McKay & W.G.Holton - J.Am.Chem.Soc.78,1618,(1956).

39. W.R.McWhinnie & J.D.Miller - Adv.Inorg.Radio.Chem. 12,135,(1969).

39a. O.Farver & G.M.Nord - Acta.Chem.Scand. 20,1429,(1966).

40. J.R.Hudman - B.Sc.Project Report Uni. ofAston.(1969).

40a. B.Martin,W.R.McWhinnie & G.M.Waind - J.Inorg.NuclearChem. 23,207,(1961).

41. I.R.Beattie,T.R.Gilson & G.A.Ozin - J.Chem.Soc.(A) 2765,(1968).

41a. W.R.McWhinne & Mary Fernandopulle. Unpublished Observation.

41b. W.R.McWhinnie & G.C. Kulasingam - J.Chem.Soc.(A) 1199,(1966).

42. W.J.Baxter & G.Gafner - Inorg.Chem. 11,176,(1972).

42a. V.A.Bryukhanov,B.Z.Iofu,A.A.Opalenbo & V.S.Shpinel - Russ. J. Inorg. Chem. 12,1044,(1967).

42b. F.Ya.Kul'ba,N.G.Yaraslavskii,L.V.Konovalov,A.V.Barsukov & V.E.Mironov - Russ.J.Inorg.Chem. 13,79,(1968).

42c. D.M.Adams & J.B.Cornell - J.Chem.Soc.(A). 884,(1967).

43. A.F.Glifford & A.G.Morris - J.Inorg.Nucl.Chem. 5,71,(1957).

44. O.Foss et. al. - Acta.Chem.Scand. 15,1939,(1961).
- Acta.Chem.Scand. 15,1615,(1961).

44. O.Foss.et.al - Acta.Chem.Scand. 16,779,(1962).
- Acta.Chem.Scand. 17,1806,(1963).

45. R.J.Gillespie & R.S.Nyholm - Quart.Rev. 11,339,(1957).

46. D.P.Stevenson & V.Schomaker - J.Am.Chem.Soc. 62,1267,(1940).

47. H.Gerding & H.Houtgraaf - Rec.Trav.Chim. 73,737,(1954).

48. D.M.Adams & P.J.Lock - J.Chem.Soc.A. 145,(1967).

49. A.Voigt & W.Biltz - Z.Anorg.Chem. 133,298,(1924).

50. A.Schmitt & W.Zeil - Z.Naturforch. 18,428,(1963).

51. G.C.Hayward & P.J.Hendra - J.Chem.Soc.(A). 643,(1967).

52. I.R.Beattie & H.Chudzynska - J.Chem.Soc.(A). 984,(1967).

53. N.N.Greenwood,B.P.Straughan & Anne.E.Wilson - J.Chem.Soc.(A). 1249,(1966).

54. N.N.Greenwood et al. - J.Chem.Soc.A. 2209,(1968).

55. R.E.Dodd, L.A.Woodward & H.L.Robert - Trans.Faraday.Soc.52,1052,(1956).

56. Bruno.Buss and Brent Krebs - Agnew.Chem.Inernat.Edi. 9,463,(1970).

57. E.Demarcay - Bull.Soc.Chim.France 40,99,(1883).

58. A.Scott - Proc.Chem.Soc. 20,156,(1904).

59. S.C.Cohen,M.L.N.Reddy and A.G.Massey. - J.Organometal.Chem. 11,563,(1968).

60. G.T.Morgan & F.H.Burstall - J.Chem.Soc. 180,(1931).

61. W.V.Farrar & J.M.Gulland - J.Chem.Soc. 11,(1945).

62. M.Schmidt & Schumann - Z.Naturforsch 19b,74,(1964).

63. W.Mack - Agnew.Chem.Internat.Ed.77,260,(1965).

64. M.Giua & F.Cherchi - Gazz.Chim.Ital. 50,362,(1920).
(chem.abstract 15-521)

65. N.Petragnani & M.deMoura Campos - Ber. 96,249,(1963).

66. K.Bowden & E.A.Braude - J.Chem.Soc. 1068,(1952).

67. W.A.Waters - J.Chem.Soc. 1077,(1938).

68. F.Kraft & R.E.Lyons - Ber. 27,1764,(1894).

69. M.Adloff & J.P.Adloff - Bull.Soc.Chim.France 3304,(1966).

70. K.Lederer - Ber. 44,2287,(1911).

71. D.Hellwinkel & G.Fahrbach - Tetrahedron Letters No.23,1823,(1965).

72. F.Zeiser - Ber. 28,1670,(1895).

73. M.Vobetesky,V.D.Nefedov & E.N.Sinomova - Zh.Obshch.Khim. 35,1684.(1965).

74. H.Taniyama,F.Moyoshi,E.Sakakibara & H.Uchida - Yakugaku Zasshi. 77,191,(1957).

75. R.B.Sandin,R.G.Christiansen,R.K.Brown & S.Kirkwood - J.Am.Chem. Soc. 69,1550, (1947).

76. R.B.Sandin,F.T.McClure & F.Irwin - J.Am.Chem.Soc. 61,2944,(1939).

77. G.T.Morgan & R.E.Kellett - J.Chem.Soc. 1080,(1926).

78. G.T.Morgan & H.D.K.Drew - J.Chem.Soc. 127.2307,(1925). ibid. 133, 2600, (1930).

79. K.Lederer - Ber. 53B,1430,(1920).

80. H.Rheinboldt & N.Petragnani - Ber. 89,1270,(1956).

81. L.Tschugaeff & W.Chlopin - Ber. 47,1269,(1914).

82. N.Petragnani - Tetrahedron - 11,15,(1960).

83. G.Wittig & H.Fritz - Ann. 577,39,(1952).

84. D.Hellwinkel & G.Fahrbach - Ber. 101,574,(1968).

85. D.Hellwinkel & G.Fahrbach - Tetrahedron Letters No.23,1823,(1965).

86. E.H.Braye,W.Hubel & I.Caplier - J.Am.Chem.Soc. 83,4406,(1961).

87. W.Mack - Agnew.Chem.Internat.Ed. 78,940,(1966).

88. M.T.Chen & J.W.George - J.Am.Chem.Soc. 90,4580,(1968).

89. G.C.Hayward & P.J.Hendra - J.Chem.Soc.A. 1760,(1969).

90. G.D.Christofferson,R.A.Sparks & J.D.McCullough - Acta Cryst. 11,782,(1958).

91. G.D.Christofferson & J.D.McCullough - Acta.Cryst. 11,249,(1958).

92. W.R.Blackmore & S.C.Abrahams - Acta.Cryst. 8,317,(1955).

93. H.P.Fritz & H.Keller - Chem.Ber. 94,1524,(1961).

94. D.Lloyd & M.I.C.Singer - Chem.&Indst. 118,(1967).

95. D.Lloyd & M.I.C.Singer - Chem.Comm. 396,(1967).

96. H.Freeman & Douglas LLoyd - Chem.Comm. 424,(1970).

97. K.Lederer - Ber. 48,2049,(1915).

98. K.Lederer- Ber. 49,1071,(1916).

99. L.Tschugaeff & W.Chlopin - Ber. 47, 1271, (1914)

100. C.R.C.Handbook of Chemistry & Physics - Edition 41.

101. J.D.McCullough & R.E.Marsh - Acta.Cryst. 3,41,(1950).

102. D.H.Whiffen - J.Chem.Soc. 1350,(1956).

103. R.C.Poller - Spectrochim.Acta. 22,935,(1966).

104. A.L.Smith - Spectrochim.Acta. 24A,695,(1968).

105. J.R.May,W.R.McWhinnie & R.C.Poller - Spectrochim.Acta 27A,969,(1971).

106. M.de.Moura Campos,N.Petragnani & C.Thome - Tetrahedron Letters, No.15, 5,(1960).

107. W.W.Moyer, T.Anyos & J.L.Dennis J.Org.Chem. 31,1094,(1966).

108. Herbert Brintzinger & Annelise Scholz. - Chem.Ber. 83,141,(1950).

109. J.F.King,A.D.Allbutt & R.G.Pews. - Can.J.Chem. 46,805,(1968).